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AUGUST, 1937

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THE ATMOSPHERIC POTENTIAL GRADIENT AT OTTAWA, CANADA¹

By D. C. ROSE²

Abstract

The atmospheric potential gradient was observed continuously at the National Research Laboratories at Ottawa for a year ending December 1, 1935, and at a country station about nine miles northwest of Ottawa, for four months ending November 1, 1936. The country station was set up on a site as free as possible from man-made pollution of the atmosphere. The records were studied from two points of view, the diurnal variation and disturbances in the normal fine weather value of the potential gradient. The results indicate that the diurnal variation is similar to that of other similarly situated stations. The study of disturbances in the potential gradient shows that all disturbances can be correlated with local meteorological conditions. The disturbances were for the most part associated with the stormy conditions usual at the passage of a front. The effect of city pollution on potential gradient records is clearly shown.

Introduction

Measurements of the electric field at the surface of the earth have been generally accepted to indicate that the surface of the earth is charged negatively. A corresponding positive charge exists in the atmosphere, and the small conductivity of the atmosphere allows a continuous positive current to flow to the earth. The maintenance of such a state of equilibrium is thought to be effected by intense reversed currents caused by thunderstorms. Wilson (21) introduced this explanation, and experiments of others (20, 22) tend to confirm his explanation at least in a qualitative way.

The potential gradient under fine weather conditions has a well observed diurnal and seasonal variation which differs somewhat in different localities. Between periods of fine weather with normal undisturbed potential gradient, there are periods in which it is disturbed or deviates in an erratic manner from its normal fine weather value. The object of the present investigation was to study the nature of these disturbed periods and their time of occurrence with respect to other meteorological conditions. As the apparatus was made to record the potential gradient continuously, the fine weather variation was also studied with a view to comparison with other such stations throughout the world.

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From December 1, 1934, to December 1, 1935, observations were taken at the National Research Laboratories situated on the north side of the city of Ottawa on the bank of the Ottawa River. Here a definite effect was found which would indicate a difference in the behavior of the potential gradient with rising and falling barometer, or with the passage of an anticyclone near the observing station. Owing to the geographic location of the observation point with respect to the city, it was impossible to tell to what extent the deviations from expected potential gradient variations were due to changing electrical properties of the air mass moving across the continent, or due to the effect of pollution from the city carried by winds under different meteorological conditions. Hence, during the late summer and autumn of 1936, a country station was operated at a point about nine miles directly northwest of Ottawa. The site was chosen as far away from inhabited buildings as possible. There was a farmhouse about one-quarter of a mile to the south and two summer cottages about an equal distance to the southeast. Observations were taken during the months from July to October inclusive, and except for domestic cooking in these houses and heating during October, there would probably be no fires. The fires used for cooking would probably be those in small wood-burning or oil stoves, which would usually be burning for only an hour or so before meal times. The village of Old Chelsea is about $1\frac{1}{2}$ miles south of the station, and small settlements of summer cottages are located about a mile to the northeast. There were no industries in any of these localities and it is unlikely that there would be any fires other than those needed for the domestic purposes mentioned above. The railway ran in a NE-SW direction about a mile to the northeast of the station, but it is only a branch line passing through small villages along the Gatineau River; there were only two or three trains a day. Apart from a few small villages scattered along the Gatineau and Ottawa Rivers and a few scattered farms, there are no large residential or industrial areas for some distance, except the cities of Ottawa and Hull and their suburbs. These are centered slightly south of southeast of the station, the nearest outskirts of Hull being about seven miles away. A 50-mile radius would include to the west, south, and east, a few towns of from 2,000 to 4,000 inhabitants, but in northerly directions the country is virtually uninhabited except for small scattered villages and farm areas along the Gatineau River and more distant lumber and mining centres in Northern Ontario and Quebec. Hence, except for the effect of the proximity of Ottawa and Hull, the air at the country station is about as free from artificial pollution as any that could be found without moving unreasonably great distances from civilization. In regard to pollution from Ottawa and Hull, the wind seldom blows from the southeast direction for any length of time, so the country station is about as well situated with respect to these cities as it could be.

The situation at the laboratories in Ottawa is such that to the north and west, except for the small village of Gatineau Point, there is no large residential or industrial area for great distances. In fact, from a line northeast from

the laboratories to a line west from the laboratories, there should lie no source of pollution of any magnitude except the laboratory heating plant (the chimney of which is about 100 yd. north from the collecting electrode) and a cement works about $1\frac{1}{2}$ miles WNW. The laboratory heating plant appeared to cause no trouble except on rare occasions when the smoke hung around the corner of the building where the electrode was situated. The plant is built on the side of a cliff below the laboratories and the elevation of the top of the chimney is about 15 to 20 ft. below the level of the collecting electrode. In fine weather the wind and eddy currents are such that the smoke is blown well away from the building before rising to the height of the electrode. Only on a few occasions throughout the year was any movement of smoke towards the electrode noted.

Apparatus

The schematic diagram of the arrangement of the laboratory recorder is shown in Fig. 1. The window through which the collector projected was about 30 ft. above the ground on the northeast end of the laboratory. The

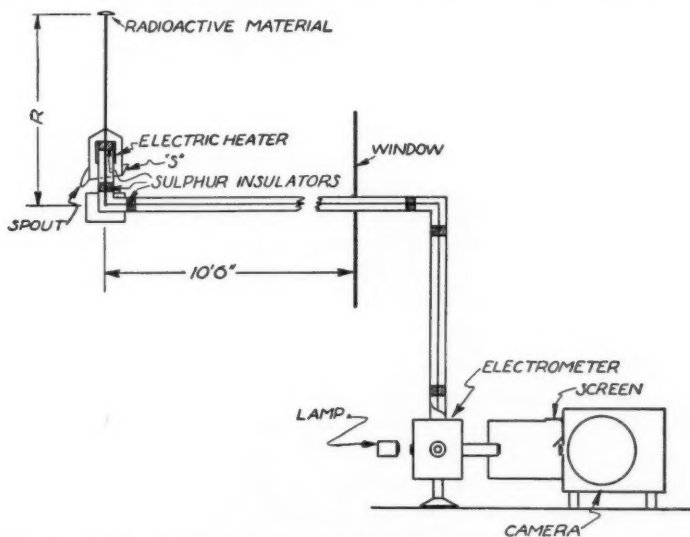


FIG. 1. Diagram of apparatus at the laboratory station.

insulation used was sulphur. The design of the weatherproof head supporting the radioactive collector system proved to be very satisfactory once the electric heater was installed. This heater consisted of a few turns of nichrome wire wound on asbestos paper around the vertical tube holding the supporting insulators. The temperature was kept a few degrees above the surrounding air temperature. The inverted skirt, *S*, surrounding the bottom of the weather shield, was an important feature in collecting rain and draining

it off through the spout in such a way that the water cleared the grounded parts. The insulation in this apparatus could be maintained in good condition through many hours of steady rain, provided that winds were not high enough to blow moisture up under the shield covering the insulators. The distance from the window to the collector was 10 ft. 6 in., and two different heights, R , were used for the collector, namely 31 and 21 in. A simpler design of collector support and insulated system not extending so far out from the window would have been equally satisfactory. This apparatus was designed primarily to support a sphere for observing potential changes when there were lightning flashes. For such observations, it was desirable to have it extend out as far as possible from the wall of the building. It proved, however, a satisfactory potential gradient recorder, except for the fact that the whole apparatus had to be withdrawn into the room to make a proper test of the insulation. This did not have to be done oftener than about once a month, because experience showed that apart from some trouble with insects in the autumn of the year and except for rare periods of exceptionally severe weather conditions, the insulation remained good almost indefinitely, and during bad weather it was either quite good or so definitely bad that there was no doubt about its behavior. Some trouble was experienced, particularly at high potential, with the accumulation of charges on the sulphur. This would have the effect of an apparent leak, when the potential was changed suddenly, which would practically disappear in a few minutes. This would introduce an error in rapidly changing potential gradients, but as under such circumstances the value could not be measured with any great accuracy this effect was not considered important. The radioactive collector was of sufficient strength that the insulated system would acquire half its final potential in less than 30 sec., and the insulation leak was always sufficiently high compared to this to cause negligible errors of registration except under extreme weather conditions. When there was any doubt at all about the insulation, the records for such periods were omitted from the analyses of the results.

A rotating drum camera in conjunction with a single-fibre electrometer was used for recording. The camera was driven by a weight, the rate being controlled by a telechron motor in such a way that it rotated once in about 26 hr. The record was changed every 24 hr. The 24-hr. record was about 29 in. long, so that one inch represented a little less than one hour. A commutator arrangement (not shown) grounded the electrometer and applied fixed positive and then negative voltages to the insulated system for a few minutes every four hours. These points were used for time reference points on the record, and the impressed voltages gave an indication of the accuracy with which the electrometer retained its calibration. The potential gradient could be observed at any time, as a mirror situated just above the cylindrical lens, which focused the fibre on the photographic paper, reflected a part of the image of the fibre on a horizontal ground glass screen and scale in the housing of the camera. The distance of this scale from the microscope was the same as that of the photographic paper, so a calibration on this scale

required no further interpretation to convert measurements, on the record, to volts. The electrometer retained its calibration with sufficient accuracy that a careful calibration about once a month was sufficient. The photographic record was three inches wide. The zero position was adjusted slightly off centre so that actual voltages from 325 positive to 250 negative could be recorded.

The same recording apparatus was used at the country station. The collector system is somewhat different and is shown in Fig. 2. The apparatus was housed in a box 6 by 3 by 3 ft., the long dimension being horizontal. The box was mounted on a frame about 3 ft. off the ground. A turret, 1 ft. square, rising vertically 3 ft. at one end of the box, supported the collector and weather proof insulated system. The collector was 9 ft. 8 in. in height from the ground. The design of the insulated system was somewhat different from that used in the laboratory. Sufficient details are given in the figure that no further description should be required here.

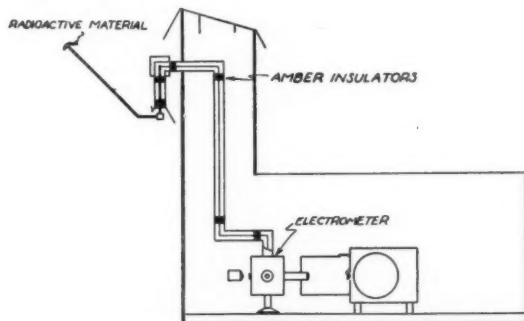


FIG. 2. Diagram of apparatus at the country station.

A radioactive collector similar to the one used with the laboratory recorder was employed. The insulation in this apparatus was amber throughout and it proved much more satisfactory than sulphur. Its insulating properties appeared to be better and no accumulation of charge in the insulators was noted. Tests were made regularly and the insulators, when charged to about 150 volts with the collector removed, showed no measurable loss of charge in periods of two minutes or so. Rain flurries did not affect the insulation, though it would usually break down after two or three hours of steady rain. It was noted that the process of loss of insulation due to moisture on the surface of the outer insulator took place and cleared in relatively short periods of time. With continued heavy rain, the insulation would remain quite good for some time, then would break down to a very low value (so low that no potential would be recorded) in the comparatively short period of half an hour to an hour. The time from effective short circuit of the insulated system to good insulation would be of the order of an hour after the rain stopped and the air became dryer. The amount of rain the system would

stand and the time required to recover after loss of insulation depended on how often it had been subjected to such conditions since last being overhauled. Complete overhaul was required only three times in the four-month period during which the station was operated. This was done by dismantling all the insulators except those in the electrometer and turning a layer off the exposed surfaces.

The camera was driven at about half its previous speed; the record was therefore changed every 48 hr. instead of every 24 hr. Between replacements of the photographic paper the apparatus ran with no attention. The time required to renew the photographic paper, test the insulation, etc., was from one-half to three-quarters of an hour. As no electric power was available at the country station an ordinary alarm clock was adapted to control the speed of the camera, and current for the illuminating lamp was supplied from a storage battery which could be used for four days without recharging.

The radioactive collector used in both the laboratory and country stations was made from old glass radon seeds, the glass being broken up and stuck on a copper plate with a layer of shellac thin enough to allow the passage of α -particles of reasonable range. A copper plate was mounted on the under surface of an inverted saucer-shaped disc of dural. This disc was supported by a 1/4 in. dural rod as shown in Figs. 1 and 2. This collector (Ra D, E, and F mixture in equilibrium) has the advantage that it is easy to obtain and its decay period is long, but the disadvantage is that it emits weak β - and γ -rays, as well as α -rays. The effect of γ -rays in causing an insulation leak in the electrometer was shown to be too small to be considered. The effect of β - and γ -rays on increasing the rate of ionization in the neighborhood of the collector would result only in a lowering of the effective height of the collector. This would cause the potential gradient readings to be low by a constant factor. Without definite knowledge of the quantity of the radioactive material on the collector, it is difficult to estimate the possible magnitude of the effect. A rough examination of radioactive data shows that the γ -rays would contribute very little once a distance of several centimetres from the collectors was reached, but β -rays would be relatively more effective in creating a general increase in ionization at a distance of a metre or two from the collector. The error would certainly not be large in the present case, as the magnitude of potentials found agrees well with other stations similarly located.

In the present investigation, variations in the potential gradient rather than its absolute value were being studied; hence no serious attempt was made to obtain a very accurate reduction factor. The reduction factor necessary to correct readings at the laboratory station to volts per metre was measured approximately by means of a portable electrometer and a wire stretched over the ice on the Ottawa River behind the laboratory. This was the largest flat area free from trees near the laboratory building. At the point where the observations were taken the river is about 1/4 mile wide and the building is situated about 100 yd. from the bank of the river.

The height of the window above the water level is approximately 75 ft. The horizontal wire was stretched about one metre above ground and was about 50 ft. long between insulated supports. A radioactive collector, probably a little stronger than that used on the registering apparatus, was placed at its centre. Observations were taken on two days for about an hour and a half about noon of each day. On the first day the potential gradient was in a disturbed state, and, while the general nature of the variations observed on the river and those recorded in the laboratory were the same, there was considerable difference in detail. For instance, a reversal in the potentials observed on the river showed up only as a reduction to about half its normal value at the laboratory. On the second day, except for a short disturbance which showed the opposite effect, that is, a reversal in the laboratory which did not appear on the potential observed on the river, the curves were parallel for an hour and a reduction factor could be estimated. The factor so found was 0.77. In view of the fact that the factor is estimated from observations extending over a single hour on one day, and in view of the difficulty in knowing the exact effective height of the collector, no great accuracy is claimed for the reduction factor. According to Scrase (16) the most reliable exposure factor is obtained by means of a test plate placed in the roof of an underground laboratory. Such a method could obviously be used only in an observatory containing such equipment. Unfortunately this reduction factor was applicable only to the results taken between December 1, 1934, and April 13, 1935, since on the latter day the rod, *R*, (Fig. 1), supporting the collector was reduced in length in order that the sensitivity of the electrometer could be increased somewhat to improve the focus of the fibre at the extreme ends of the scale. To compare the results before and after this change, a factor (apart from electrometer sensitivity corrections) was used which was merely the inverse ratio of the lengths of the insulated rod from the centre of the head (Fig. 1) to the collector. There is no justification for the procedure except that the annual variation curve (Fig. 3) shows no greater discontinuity between April and May than between some of the other consecutive months. There was a disturbance during virtually all the latter half of April, so the value for April was obtained practically entirely from observations made during the two weeks before the change was made. No attempt was made to obtain a reduction factor for the country station.

In reading the records, the zero line was drawn by joining the points on the record where the electrometer was grounded. Hour marks were indicated and the deflection was measured by scaling with a steel scale divided in half millimetres. Measurement could be made to 2 or 3% when the potential gradient was steady, but under ordinary daytime conditions small rapid variations usually occur, which make it difficult to measure the exact value from the record to better than from 5 to 10%, depending on the magnitude of the deflection at the hour concerned. With this in view, to save time in measurement, readings were taken to the nearest half millimetre deflection of the electrometer. Instead of obtaining a true average by estimating

the average of the potential for an hour centered about the time for which the reading is tabled, the value used for each hour was the actual value at that hour. This method was adopted as it appeared more suitable for the

study of potential gradient disturbances discussed in the latter parts of this paper. Where fluctuations were so great in magnitude and rapidity that a spot reading could not be obtained, the mean over a period of from five to ten minutes before and after the hour was estimated and entered as the value at that hour. The time marks and the setting of the clock were kept with such accuracy that the probable error in location of hour marks would never be greater than two or three minutes difference from Eastern Standard or 75th meridian time.

Results

DIURNAL VARIATION

Fig. 3 shows the diurnal variation means for each month, except August, at the laboratory station. The author was absent for the greater part of August and the apparatus was not operated. Fig. 4 shows similar curves plotted to a larger scale for the four months in 1936 during which the country station was operated, the mean for the four months, and the mean for the year at the laboratory station. Owing to the fact that the reduction factor was known only approximately, these results are plotted as per-

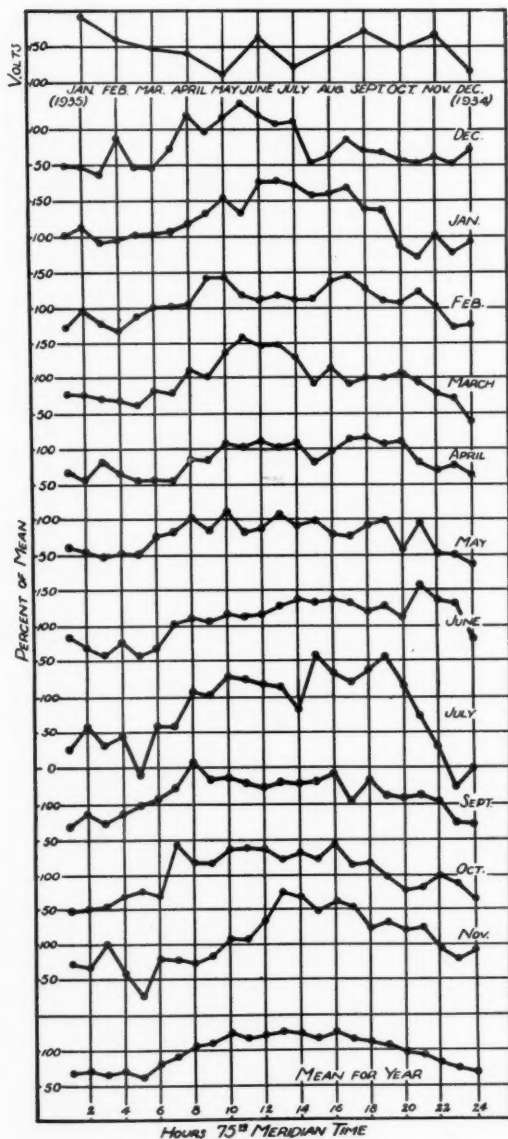


FIG. 3. Annual and diurnal variation at the laboratory station.

centages of the mean rather than in volts per metre. The mean value of the potential gradient for the year at the laboratory station, using the approximate reduction factor discussed above, was found to be 118 volts per metre. These curves represent observations taken during fine weather conditions only. In the case of the country station the curves include practically all observations, except those taken during obviously disturbed or stormy conditions. In the case of the laboratory station, a different criterion was used. The hourly readings were taken for every hour at which a reading could be obtained, that is, omitting only hours when the insulation was bad, the potential was so high that the fibre was off the scale, or the fluctuations so great and so rapid that no reading could be obtained. These were averaged for periods of half a month, and a smooth curve drawn through the points was thus obtained. The differences between the individual hourly observations and points picked from the smoothed curve were plotted. Such a curve is shown in Fig. 5. The differences were plotted without respect to sign for the sake of convenience. When these differences were less than 150 volts (not corrected by reduction factor) for a period of four hours or more, the readings were taken as representing undisturbed conditions. This practically limits readings to periods of rising barometer and winds in the north to

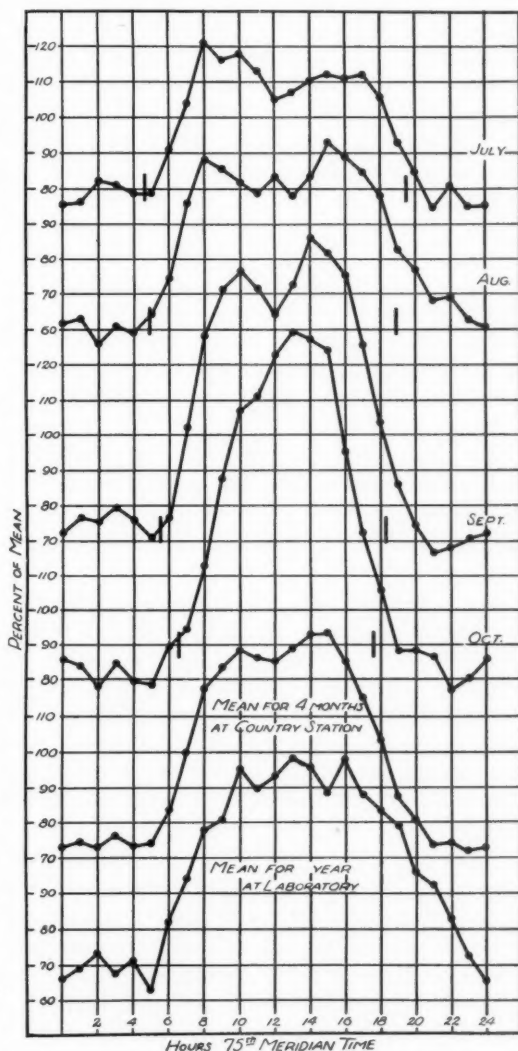


FIG. 4. Diurnal variation at the country station, and mean for year at the laboratory station

west quadrant. The reason for this is discussed in a later section on potential gradient disturbances.

The diurnal variation is in general agreement with most similarly situated stations at various places throughout the world. The diurnal variation of the potential gradient over land usually contains an early morning minimum, a morning maximum, a daytime minimum, and an evening maximum. This variation is considered to be made up of local effects superimposed on the well known world time variation which is observed at sea. As shown by Mauchly (12) the mean diurnal variation curve at sea has a total variation of the order of 30% of its mean value, and a single maximum at approximately 14 hr. 75th meridian time. Hence, in the curves shown in Fig. 4 the daytime minimum is less pronounced and the afternoon maximum is somewhat enhanced by the effect of the universal time variation. The results at the country station show that this enhancement is more noticeable in September and October where the universal time maximum and the afternoon maximum more nearly coincide than in July and August. The monthly mean curves shown in Fig. 3 were too erratic to justify plotting on the large scale used in Fig. 4, and the effects of the universal time variation and the definite morning and afternoon maxima are correspondingly less pronounced. This is not unexpected when the total times during which the potential gradient could be considered undisturbed are compared at the two stations. Table I, Columns 2 and 5, shows the number of hours each month for which the potential gradient could be considered to be undisturbed. Columns 3 and 6 show this same number in percentage of the total number of hours the station was operated. The difference in the values at the laboratory station and at the country station are apparent.

TABLE I
HOURS OF UNDISTURBED POTENTIAL GRADIENT

Month	No. of hourly observations	% of hours station was operated	Month	No. of hourly observations	% of hours station was operated	Monthly mean volts
1934 <i>Laboratory station</i>			1935 <i>Laboratory station</i>			
Dec.	128	22	Sept.	184	26	
1935			Oct.	191	28	
			Nov.	176	25	
Jan.	181	26	1936 <i>Country station</i>			
Feb.	133	20	**July	691	85	120.7
Mar.	141	19	Aug.	538	72	107.6
Apr.	113	17	Sept.	461	68	136.3
May	199	31	***Oct.	435	54	143.2
June	160	23				
*July	79	19				
Aug.	—	—				

*July 1 to 20 only. **June 26 to July 31. ***Oct. 1 to Nov. 3.

It is generally considered that the potential gradient at the earth's surface is caused by the fact that the potential of the high conducting layers in the atmosphere is raised above that of the earth either by charges carried upwards during thunderstorms or by some unknown means. The fact that the air is continuously being ionized by radioactive matter in the air, cosmic rays, etc., means that a space charge is set up. The properties of the ions producing the conductivity and magnitude of the effects involved are such that the space charge is mainly concentrated near the surface of the earth, the potential gradient decreases, space charge decreases, and conductivity increases rapidly with height above the earth's surface (2, 3, 7). Hence, at the earth's surface, the potential gradient would be expected to depend to a great extent on local conditions which affect the ionization equilibrium. For the present the effect of rain, charged clouds, etc., which represent disturbed conditions, will be omitted, and will be discussed in the next section of this paper.

The fundamental variables which control the potential gradient are considered to be: i , the air-earth current; λ , the conductivity; F the potential gradient, the equation $F = \frac{i}{\lambda}$ being supposed to hold at the surface of the earth. If one accepts the Wilson theory that the atmospheric electric phenomena are due to the transport of charges by thunderstorms to high conducting layers in the atmosphere, then the potential gradient would be expected to depend on this phenomenon. On the other hand it is well known that the conductivity depends on the rate of production of ions, q , the number of condensation nuclei, Z , and the conditions of equilibrium between production and loss of small ions, formation of large ions, etc. In localities where the number of condensation nuclei is relatively unimportant, such as at sea, and in polar regions, the universal time variation in potential gradient has been shown by Whipple (19) to agree with an estimation of the time variation in thunderstorms throughout the world. Whether this is a sufficient explanation of the universal time variation in F would depend on the nature of variations in the rate of ionization, q , at the surface of the earth. This is a difficult quantity to measure directly, but some experiments indicate that it cannot be treated as constant. Nolan and Nolan (13, 14), from indirect calculation of q , show that its diurnal variation resembles that of the potential gradient, and Hogg (9, 10) has indicated the possibility of a universal time variation of the rate of ionization which is in phase with that found for the potential at sea. Hence, we have two possible and independent explanations of the universal time variation in potential gradient.

The effect of condensation nuclei on the potential gradient is due to the effect of nuclei on the conductivity. The equilibrium relations between small and large ions, nuclei, etc., have been discussed by many investigators. In thickly populated areas and to a lesser extent in rural areas, the effect of nuclei is far more pronounced than the effect of variations in the rate of production of ions or in the air-earth current. Qualitatively the effect of nuclei is described by Scrase (16). The explanation of the double peak in the

diurnal variation curve found at Kew was advanced by Simpson, and is as follows: Smoke (from domestic and industrial sources) increases from about 5 hours until 9 hours, and, as convection during this period is small, pollution increases rapidly; this results in an increasing potential gradient. During the day, convection is greater and the air near the ground is cleared at the expense of the air higher up. During the evening the reverse is true and a second maximum appears.

In Fig. 4 the approximate times of sunrise and sunset are marked for the middle of each month, and it is noted that the potential gradient starts to increase immediately after sunrise. The afternoon maximum for September and October is more prominent than the morning maximum, though in the case of July, August, and the mean for the year it is of approximately the same magnitude. A longer series of observations would, of course, be necessary to decide whether or not this has any real significance. If a true separation of the universal time variation and the local variation could be made, the afternoon maximum would probably be less than the morning. If the approximate method given by Brown (4) to make such a separation is used this appears to be the case. Brown also collected results from several places throughout the world and these show considerable differences in the relative heights of the morning and afternoon maxima. For instance, Allen (1) found virtually no afternoon maximum at Mount Stromlo, while at other places it is equal in prominence to the morning maximum. The above explanation of the reason for the diurnal variation does not explain these differences.

That separate effects due to artificial and natural pollution are apparent is shown by an examination of stations like Kew. That the effect here is mostly due to artificial contamination is apparent from the fact that the position of the morning maximum varies less with the seasons than at many other places, and it moved forward an hour at the advent of daylight saving time (16). The observations at the country station described here show such a consistent variation with the time of sunrise that the effect would seem to be entirely natural. The same variation with sunrise is shown by Allen (1) at Mount Stromlo, but only to a lesser extent at Hotel Canberra. In the case of Johannesburg, Halliday (8) shows a variation in time of morning maximum which tends to follow the time of sunrise during the months from April to November, and then some other influence becomes prominent which makes the morning maximum late and the evening maximum irregular. The explanation of these differences, no doubt, lies in differences in pollution due to different situations with respect to sources of pollution and to local meteorological conditions.

Wait (18) made a series of observations for a short period in 1929 at a station remote from any industrial centre at Penalosa, Kansas, about the geographical centre of the United States. The results indicate a curve fitting very closely in phase and relative magnitude to the diurnal variation found over oceans when plotted in universal, rather than local, time. In the present experiment

at the country station northwest of Ottawa, though different results were obtained, it would be expected that the amount of man-made pollution would be almost as small as at Penalosa. The same probably applies to the several other stations such as Mount Stromlo, if one can take the regular movement of the position of the morning maximum with the time of sunrise as an indication of lack of man-made pollution.

Brown has classified stations according to latitude, and observes corresponding differences based on the shape of the curve after separating the universal time variation. That a classification according to latitude is natural is seen when one considers the variation in time of the morning maximum. If it follows sunrise at all stations, the result will be a different diurnal variation at different latitudes when averaged over a year. He also finds two types at mean latitudes, a broad type and a narrow type. In the case of five out of the six stations showing the broad type he points out that the station was probably situated in locations subject to considerable man-made pollution.

In conclusion, it may be stated that the results of the present observations agree in general with others. Detailed comparisons as outlined in the above paragraphs with other stations show differences which will probably require simultaneous observations of complete local meteorological conditions as well as other atmospheric electrical quantities at several stations for a complete explanation.

ANNUAL VARIATION

Owing to the uncertain value of the reduction factor, the annual variation curve shown in Fig. 3 (laboratory station) has no great significance except that it shows that the annual variation is not great. The curves show voltages and are not reduced to volts per metre (see paragraph on reduction factor). The general shape of annual variation curves at other stations shows a higher value in winter than in summer (8, 16). This would be expected to be particularly prominent at stations like Kew, where the influence of fires for domestic heating is felt. In the present case, owing to the location of the laboratory with respect to the city and the criterion used to select records to be included in the curve, the effect of city pollution should be small. The deviations from the mean value for the laboratory station when compared with those for the country station show that the effect of city pollution was not entirely eliminated, but the effect of increased use of fires for heating during the winter would be expected to be compensated somewhat by the blanket of snow which covers the ground from about mid-December until mid-March. A certain number of the nuclei which affect the gradient must come from the ground. When the ground is covered with snow, virtually none of these would be stirred up, and the snow blanket would act as an absorber of any nuclei which settled on it. The means for the four months during which the country station was operated are shown in the last column of Table I. They show a tendency to increase towards winter but the station was closed before any snow fell. It is unfortunate that work at the country station

could not be carried on through the winter to obtain more information on the effect of a snow blanket on the diurnal curves in Fig. 4, as well as on the annual variation.

POTENTIAL GRADIENT AND AIR MASS ANALYSIS

Little can be said from these observations about differences in the fine weather value of the potential gradient and different types of air mass. The air mass at Ottawa is usually Polar Continental or Transitional Polar Continental, the dividing line between these being not very definite, particularly in summer. Occasionally there is an inflow of different air from more tropical regions, or a recession of a mass of polar air which has moved down from the northwest and then moves back from a southwesterly direction. Southwest winds also occur which are usually associated with the passage of a barometric depression, but under such circumstances stormy conditions usually prevail and the potential gradient is disturbed owing to rain, excessive turbulence, etc.

Lansberg (11) found differences in the nuclear content with different air masses, and corresponding differences in the potential gradient would be expected. This is particularly true in view of the great differences in moisture content of polar and tropical air masses. The increased moisture content of air masses which have remained over such areas as the Great Lakes for some time would also be expected to affect the potential gradient. An examination of weather maps showed only four or five cases of a definite movement of an air mass from the south or southwest in the four months during which the country station was operated; that is, apart from periods when a definite weather disturbance was passing. One such case is described in detail in the next section, September 22 to 26, Fig. 7. An examination of this case showed that the potential gradient on September 22 and 23 was, for the most part, higher than the mean for the month. The same applies to one other day on which there was air movement from the southwest. On one day the potential gradient was definitely low during southwest winds, and other periods show no consistent difference. The small number of data here are not considered to be sufficient to give definite information on this point.

DISTURBANCES IN THE POTENTIAL GRADIENT

It is well known that stormy weather has an important influence on the potential gradient. Dust storms are reported to cause high negative potentials and its effect on potentials during thunderstorms has been definitely shown. Rain is also known to be charged, and, hence, has an effect on the potential gradient. On the other hand, clouds, except cumulus clouds under certain conditions, appear to have no appreciable effect on the potential gradient.

As stormy weather conditions in the climates at this latitude are usually associated with instability created at the "front" separating air masses of different properties, it would be expected that atmospheric electric phenomena would be considerably disturbed at the passage of a front over the station, or

while being influenced by an overhead frontal surface due to overrunning air. The potential gradient observations taken at the laboratory and at the country station were examined with a view to studying the relations between the potential gradient disturbances and the passage of fronts. For the six months of the year the laboratory station was operated, and for the four months that the country station was operated, weather maps* were obtained showing the frontal systems over Canada and the United States. The comparison of the potential gradient records with the weather maps shows that disturbances always occur at the passage of a front, and, in fact, practically all disturbances in the potential gradient where observations were completed can be explained by local meteorological conditions.

The effect of the front in producing a potential gradient disturbance is best shown by plotting deviations from the mean diurnal variation. To do this the hourly means, including all hours when a reading was obtained, covering periods of half a month were plotted. A smooth curve** was drawn through the points, and the hourly values so found were subtracted from the individual hourly readings. The differences were plotted on a time scale and placed parallel to the barograph record for comparison. The differences were plotted without respect to sign for the sake of convenience. In using hourly rather than a shorter interval between readings, disturbances of less than an hour in length would be missed if they occurred between readings. In disturbed periods, oscillations of the potential gradient over a wide range may take place in a few minutes, but as the disturbed period virtually always lasts several hours and the detailed shape of the disturbance was not being studied, hourly readings seemed quite satisfactory to show the required effect. In fine weather, isolated disturbances of less than an hour's duration rarely occur.

Before examining the figures showing samples of the disturbance found at the passage of fronts, consider what would be expected from general knowledge of potential gradient behavior discussed previously. First, the amount of disturbance in the potential gradient would be expected to bear some relation to the amount of instability in the air at the passage of the front. This will depend on the strength of the front and how near a wave in the front containing a low is to the point of observation. In an idealized system like that shown in textbooks on meteorology (5) in which a warm front is followed shortly by a cold front, one would expect no disturbance in the potential gradient until the nimbus clouds at the warm front passed overhead. The potential gradient would become normal again when the warm sector was overhead and again be disturbed when the cold front passed over. In fact one would expect only disturbances due to rain and increased turbulence at the passage of the fronts, perhaps complicated by the electrical disturbance

*These maps were borrowed from the Dominion Meteorological Office, Toronto. The author wishes to thank the Director, Mr. J. Patterson, for his assistance in giving meteorological information.

**In the case of the country station the points fitted a smooth curve sufficiently closely that they were used rather than the smooth curve.

produced by an occasional thunderstorm. If the normal balance between ionization and nuclear content were different in the different air masses, of course a different steady value for the potential gradient would be expected while the warm sector was overhead. Actually fronts do not often appear in this ideal manner but are usually much more complicated. Often several fronts of different types and of greater or less strength pass over the point of observation in a few hours.

To separate the effects of rain, thunderstorm, and generally increased mixing by turbulence would require much more detailed meteorological observations than were taken. The work of Nolan and Nolan (13, 14) would indicate that the effect of rain would be complicated, depending largely on the relative numbers of drops of different sizes. On the average, small drops were found by Nolan and Nolan to carry negative charge and large drops positive, but the space charge set up thereby is complicated by the relative rates of fall of drops of different sizes. Added to this there is the fact that charged rain actually puts charges on the exposed collector, and also the possibility of charges being generated by the breaking up of water drops striking the collector. Of course as the water drops off, a charge is carried away but not necessarily of the same magnitude as that given to the collector by the incident rain. To try to estimate the effect that charges carried to the collector by rain would have on potential gradient readings the following rough calculation was made. On the assumption that the action of the radioactive collector could be treated as a resistance connecting the collector to an equipotential surface at the potential the collector would reach under ideal conditions, a calculation of the value of the resistance can be made from the capacity of the insulated system, and the time it takes the potential to reach say within $\frac{1}{e}$ of its final value after the collector is grounded. The capacity, though not measured, is estimated at $50 \mu\mu\text{f.}$, and the time for the potential to reach within $\frac{1}{e}$ of its final value was less than one minute with the collector used. This would indicate a resistance of 1.2×10^{12} ohms or less. Now, the current flowing to the electrode because of rain may be calculated for a hypothetical case where all the rain was retained in the collector and supporting rod, so that all charge acquired from the rain would be retained. On the assumption of a rainfall of 0.5 mm. per hr. and a charge of 0.5 e.s.u. per gm.* the current flowing to a collector of projected area of 60 sq. cm. would be 1.4×10^{-13} amp. Obviously the collector used would cope with this amount of rain without any great error in potential reading. On the other hand, the effect of rain in splashing against the collector and producing charges by the Lenard effect may create considerable error in potential gradients, particularly in heavy rain. Nolan and Nolan (13, 14) in studying ionization and nuclear content find evidence of such an effect, so this should be included among the complications involved in discussing the measurement of potential gradient during rain. According to the Lenard effect the breaking up of rain drops in air causes the formation of negative ions, the drops retaining a

**Smithsonian Physical Tables, Eighth Revised Edition, page 598.*

positive charge. Nolan and Nolan also found a large increase in negative ionization during heavy rain which may be due to splashing. No attempt was made to investigate this effect in the present case, though it might be expected to show excessive positive gradients.

The effect of thunderstorms near the apparatus is of course well known. The potentials during thunderstorms are so high and variable that when such a storm was near, either the fibre would be off the scale or fluctuating too rapidly to leave a measurable photographic record.

Occasionally a front may pass the station carrying no nearby depression wave and without precipitation. In such a case the change in wind direction and velocity would be expected to have an effect on the potential gradient.

Besides the above-mentioned effects, continued rain for several hours destroyed the insulation. Hence, detailed observations throughout the passage of the front were not always obtainable. The results obtained indicate, however, that there is no characteristic behavior of the potential gradient at the passage of a front. Sometimes it stayed off the positive end of the scale for a few hours, sometimes off the negative end, and it often oscillated irregularly over a range from several hundred volts above its normal value to several hundred volts below. In view of the failure of the insulation during extreme weather conditions, it did not seem worth while to make a detailed statistical study of the magnitudes or times of positive and negative deviations from normal values during disturbed periods. For this reason as well as for greater convenience, the deviations from the mean are plotted without respect to sign.

Barograph records were taken and for part of the time at both stations a recording thermometer was operated. Weather notes were taken usually twice each day, at about 9 hours and 17 hours. As only part of the author's time was available for this investigation these are not as detailed as might have been desired. Further, notes taken in Ottawa would not be applicable in detail to the country station, particularly in regard to times of rainfall. In circumstances characterized by local thunderstorms or rain flurries often just after the passage of a cold front (such as instability in the new air mass or overrunning air from the warmer air mass), storms appear to occur at the country station much oftener than, and not necessarily at the same time as, at Ottawa. In fact from casual observation it seems likely that the average rainfall at the country station would be considerably higher than in Ottawa, though the station is only about eight miles away and of about 300 ft. higher altitude. No definite rainfall data were obtained on this point.

From a study of the daily weather maps published by the Dominion Meteorological Office, other maps showing movements of fronts, and the weather notes taken, practically every potential gradient disturbance at the country station can be explained by local weather conditions. At the laboratory station the same appears to be true but the effect of pollution from the city is added.

DESCRIPTION OF FIGURES SHOWING THE POTENTIAL GRADIENT
DISTURBANCES AT THE PASSAGE OF A FRONT

In Figs. 5 to 11 the deviation from the means are plotted in actual volts observed, no reduction factor having been used. When the disturbance was such that the image of the electrometer fibre was off the scale or moving over large voltage ranges so rapidly that no photographic trace was obtainable, the difference is shown as being off the scale on the figure, *i.e.*, higher than 300 volts. Where such a condition existed for several hours, short lines at the top of the graph are shown to indicate that the reading was off the scale continuously. The ordinate may be taken as representing the magnitude of the disturbance in the potential gradient. The barometer record is plotted above the potential deviation and weather maps below showing the approximate position of fronts at 8 a.m. on the days concerned. Only the region including the Great Lakes up to James Bay and the eastern states is included. Ottawa is shown by the black spot slightly right of centre. Centres of low and high pressure are marked *L* and *H*, and in some cases when they occurred just off the area covered by the map they are shown in a circle with an arrow-head pointing in the direction in which they are located. No distinction is made on the map between cold and warm fronts as there appeared to be no difference in the effect on the potential gradient, except perhaps in the time and duration of disturbance due to the different slope of the frontal surface. The usual motion of air masses in this district is a series of anticyclones moving in from the northwest or west, and if a depression in a front moves in such a way that a warm front passes Ottawa it is usually followed rapidly by a cold front. As there is an infinite variation in strength, shape, rate of motion, etc., of fronts and potential gradient disturbances are correspondingly different, it is difficult to generalize; hence, several examples are shown below and each described briefly.

Fig. 5, July 21 to 24, 1936, Country Station

The potential gradient deviation on the first two days is typical, in the undisturbed state, of anticyclonic fine weather conditions. On the morning of the 21st the sky was clear except for some cirrus clouds; there was a slight haze and light northerly winds. During the afternoon alto-stratus clouds were forming. On July 22 the sky was partly overcast with alto-stratus and cumulus clouds; there was no wind in the morning but there was a light southwest wind in the afternoon. A small potential gradient disturbance occurred during the morning. This is perhaps due to a change in wind direction, or to a rising wind. Such a weak disturbance in the potential gradient is sometimes noted as an anticyclone centre passes over involving a change in wind direction. A system of two fronts, the first being quite weak, was approaching from the west. The first front passed during the morning of the 23rd but the potential gradient disturbance started much earlier. Rain fell early in the morning, perhaps starting at the time of the first disturbance in the potential gradient. The weather did not clear to any extent until after the passage of the second front early on the 24th, though for a time on the 23rd

the overcast sky tended to clear and rain fell only for short periods. On the morning of the 24th the sky was completely overcast with nimbus clouds. The rain stopped during the morning. The wind shifted to NNW, the barometer started to rise, and the sky began to clear—typical of the passage of a cold front. The potential gradient disturbance cleared shortly after the passage of the front as shown in the figure.

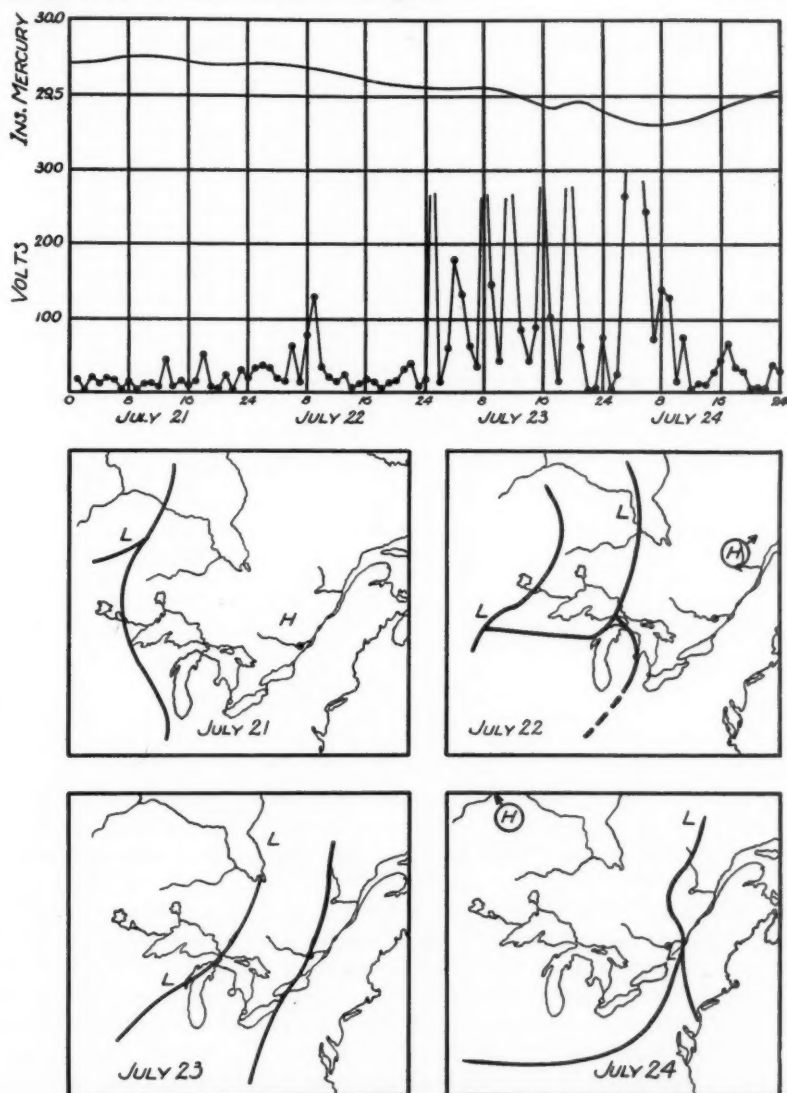


FIG. 5. Potential gradient disturbances and weather map, July 21-24, 1936, country station.

Fig. 6, August 9 to 11, 1936, Country Station

This is an example of the passage of a front without precipitation. A shallow centre of low pressure in the front passed over northern Quebec, causing only an overcast sky and no rainfall at Ottawa. The morning of August 9 was clear but hazy. Cirrus- and alto-stratus and cumulus clouds appeared to form in the afternoon with southerly winds and still considerable

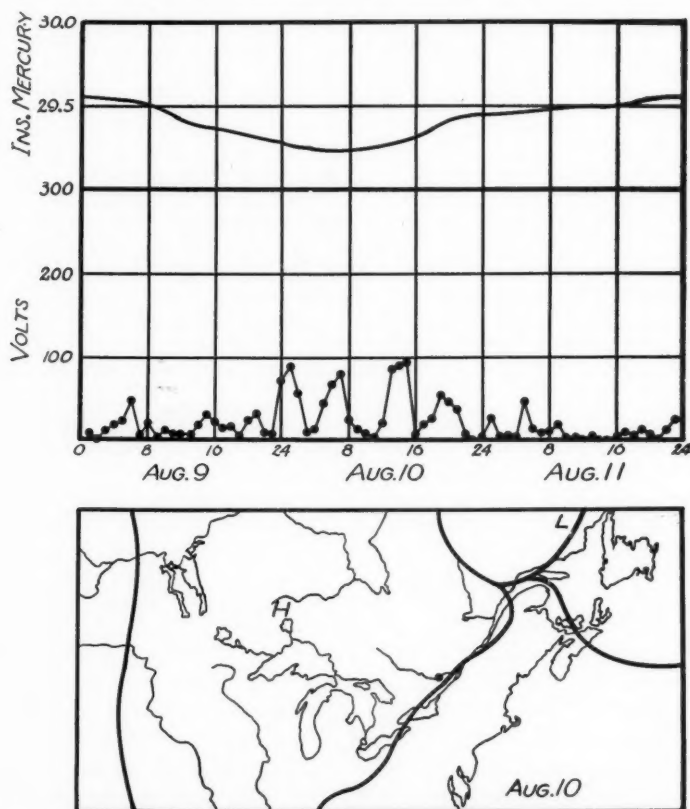


FIG. 6. Potential gradient disturbances and weather map, August 9-11, 1936, country station.

haze (visibility about 7). On the morning of August 10 the wind had shifted to NW, the sky remained mostly overcast until late afternoon when it became practically clear, and visibility improved (about 9). The potential gradient shows disturbances not of very great magnitude; most of the time the sky was cloudy. As some rather large cumulus clouds were noted it is possible that part of this disturbance was due to charged clouds, but with the data available it is impossible to separate the effect of charged clouds from increased mixing due to turbulence at the passage of the front.

Fig. 7, September 22 to 25, 1936. Country Station

On September 22 at 8 a.m. there was a weak centre of high pressure over the southeastern states and another north of Lake Huron. The movement of air was from the south, as a warm front was indicated on the map for September 22 (not shown) running east and west through Lake Huron north of Ottawa. On September 23 the sky was clear of clouds with light south wind and considerable haze. The warm front had moved farther north, its position being shown on the map for September 23. A low pressure centre

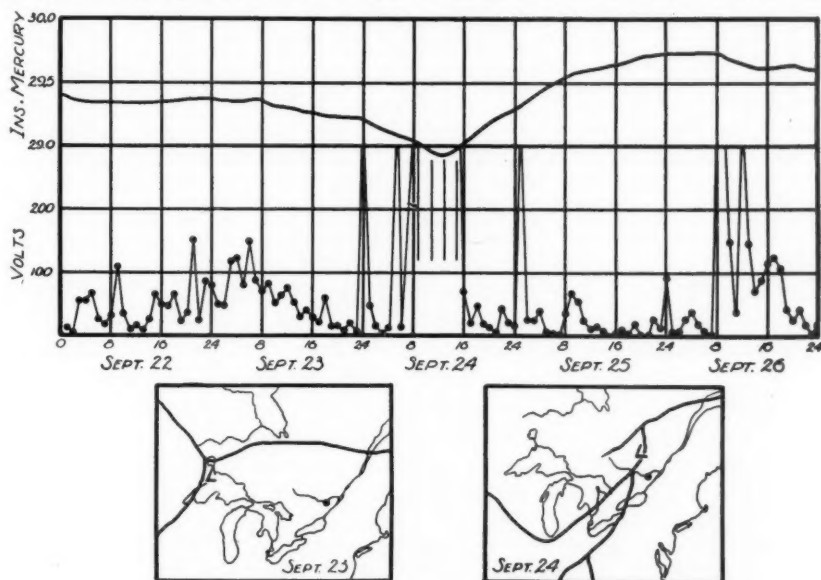


FIG. 7. Potential gradient disturbances and weather map, September 22-26, 1936, country station.

was moving in from the west. An air mass moving up from the south is not very usual in this part of the world, and the potential gradient was in a slightly disturbed state as the figure shows, even though there was no near frontal disturbance. Whether or not this disturbance in the potential gradient is due to the effect of a fundamental difference in the electrical characteristics of an air mass moving up from the south, in that it would be more moisture-laden, or the effect of greater density of population, is uncertain. The history of this air mass is probably different from that of the more usual mass moving in from the northwest only, in that it has gone farther south and then receded. The depression moving in from the west passed on September 24, accompanied by the usual potential gradient disturbance. Rain flurries and thunderstorms were noted on the 24th. By the morning of the 25th the sky was clearing again and the wind was NNW as a centre of high pressure covered most of the eastern part of the continent.

The potential gradient variation on the 26th is included in this figure to show an effect similar to that noted in Fig. 6, namely, a disturbance in the potential gradient at the centre of an anticyclone during fine weather when the sky was clear. This occurred only a few times in the four months during which the country station was operated. In this particular case the change in wind direction as the centre of high pressure passed was from a north-westerly direction to a southeasterly direction. As Ottawa and Hull lie southeast of the station it is not unlikely that this disturbance was due to pollution from those cities.

Fig. 8, October 9 to 13. Country Station

On October 9 at 8 a.m. the weather map showed a complicated system of fronts to the northwest of the Great Lakes. A centre of high pressure was located just south of Ottawa. Early in the morning of the 9th the electro-

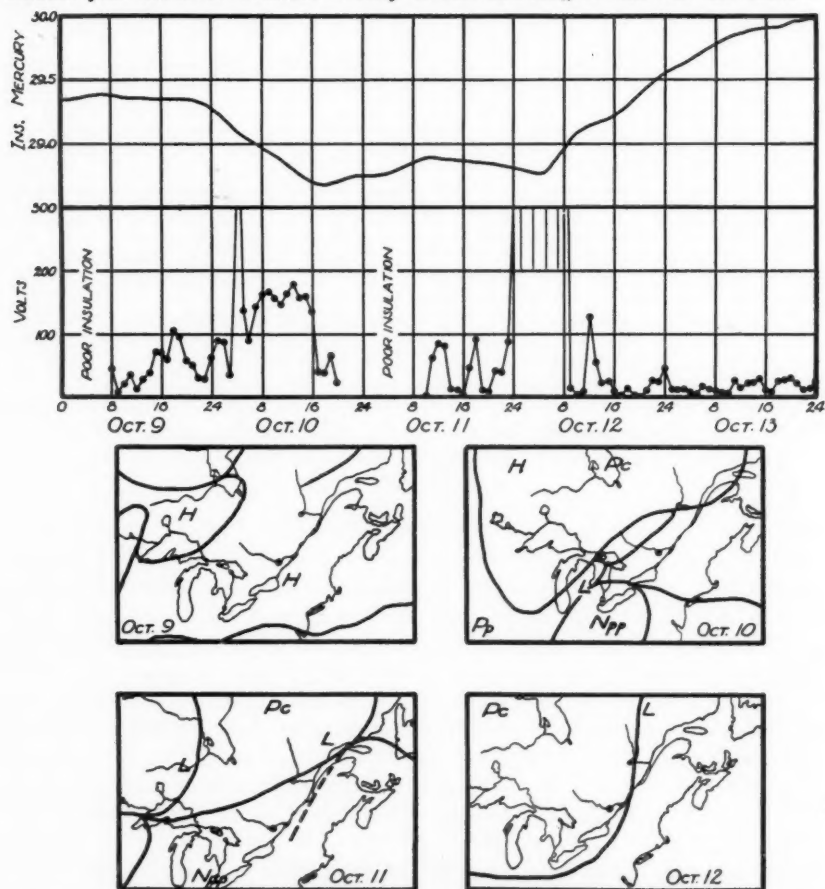


FIG. 8. Potential gradient disturbances and weather map, October 9-13, 1936, country station.

meter was grounded so the record is incomplete. The sky was clear on the morning of the 9th; cirrus- and alto-cumulus clouds formed in the afternoon. The potential gradient became disturbed as the barometer started to fall rapidly, and on the morning of the 10th the sky was overcast and rain was falling. During the afternoon the sky became broken, and showed some towering cumulus clouds, and there were rain flurries. The system of fronts that passed, as is shown by the map for the 10th, is too complicated for detailed analysis. The potential gradient disturbance was not as great as usual for so near a passage of a centre of low pressure, as the electrometer fibre was driven off the scale only for a short period. During the night of the 10th rain fell steadily and the insulation broke down. During the 11th the sky was overcast with stratus clouds, but the visibility had become very good and fresh westerly winds were blowing, typical of the weather after the passage of a front. However, another front was approaching, which passed early in the morning of the 12th. Some snow fell and the potential gradient was disturbed. After the passage of this front the barometer rose very rapidly, the sky was clear except for numerous small fracto-cumulus clouds (visibility 9) and strong northwest winds were blowing. This situation continued throughout the 13th and the potential gradient deviation from the mean was abnormally low and steady.

Fig. 9, January 11-15, 1935. Laboratory Station

A front had passed late on the 10th, and the barometer was rising rapidly on the 11th as a centre of high pressure moved in from the northwest. The sky was clear with northwest winds and the potential gradient correspondingly undisturbed. On the 13th the anticyclone was to the north of Ottawa as shown on the accompanying map. The potential gradient became disturbed as the centre of high pressure passed and remained disturbed until after the passage of the front. This is typical of its behavior at the laboratory station, that is, in most cases the potential gradient became disturbed as the wind shifted from northwestern to the eastern or northeastern quadrant. At the country station the potential gradient in most cases did not become disturbed until the new front was sufficiently near to have nimbus clouds overhead. In the present case snow started to fall about noon on the 13th though the sky was overcast all morning. The front passed about midnight on the 13th and the potential gradient became normal shortly afterwards. On the morning of the 14th the sky was clear except for some cirrus clouds and the visibility very good. The weather map showed a large anticyclone covering most of the continent. This situation did not last long as a weak front formed in the anticyclone. The map for the morning of the 15th (not shown) shows a centre of low pressure over Lake Huron. The corresponding barometer depression and disturbed potential gradient is shown in the figure. Again in this case the potential gradient disturbance started at the time of maximum barometer pressure and lasted until after the passage of the front.

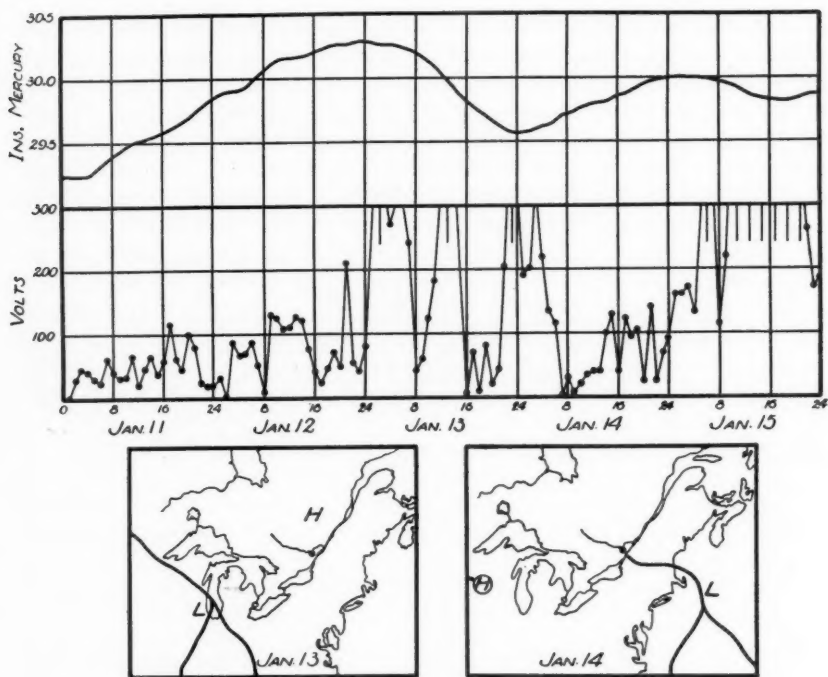


FIG. 9. Potential gradient disturbances and weather map, January 11-15, 1935, laboratory station.

The explanation of the difference between the time of start of the disturbance in the potential gradient at the two stations is considered to be in the location of the laboratory with respect to the surrounding residential area. As mentioned before, winds in the north to west quadrant should not bring pollution. This will be shown in more detail later.

Fig. 10, April 28 to May 1, 1935. Laboratory Station

On April 27 a barometric low was approaching from the west, the centre of which passed north of Ottawa early on the 28th as shown by the barometer record and the accompanying map. The low involved the movement of two or three fronts, the last of which appeared to pass during the morning of the 28th. The sky on the 28th was partly overcast with fracto-cumulus clouds, the air clear, the wind northwest. The potential gradient disturbance passed with the front, but as another low was forming to the west of the Great Lakes it did not remain undisturbed for long. The potential gradient disturbance associated with the low started even before the barometer reached a maximum, and it remained disturbed until well after the passage of the front on the 30th. The map for the 29th is not shown, as it adds but little to the description. The system of fronts which was over the eastern states

and Canada on the 28th had passed out over the Atlantic. The low west of the Great Lakes had moved over Lake Superior and Lake Huron and had developed a little longer occlusion. There was considerable rain during the afternoon and night of the 29th, so much that the insulation failed for a few

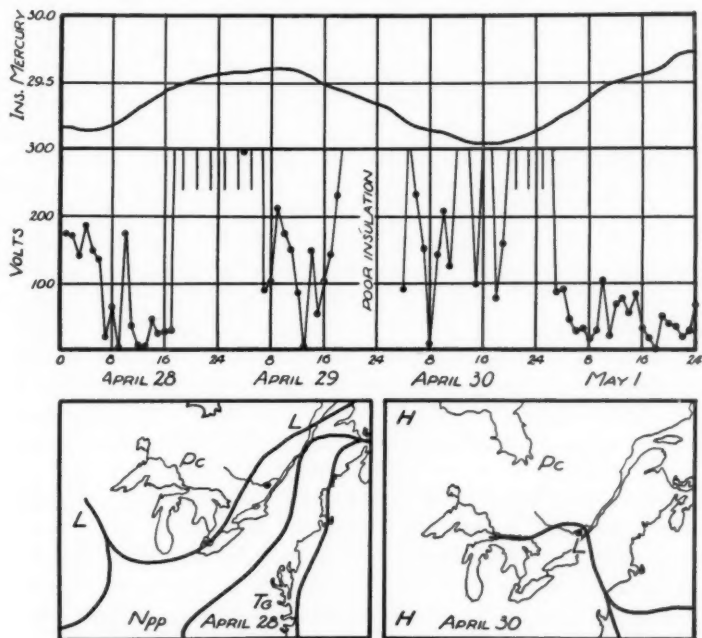


FIG. 10. Potential gradient disturbances and weather map, April 28-May 1, 1935 laboratory station.

hours. During the 30th, precipitation also fell intermittently, sometimes as snow. The front passed early on the 30th; the bent back occlusion shown on the map for the 30th kept the weather and the potential gradient disturbed until early on May 1. The sky cleared during the morning of the first with a fresh west wind and the potential gradient deviation became steadily low, typical of polar continental air moving in from the northwest.

Fig. 11, June 22 to 25, 1935. Laboratory Station

In this case the weather maps showing the position of fronts were not consulted. The barometer, the usual daily weather map showing centres of low and high pressure, etc., the potential gradient record, and weather notes, tell what was happening. On the 22nd at 8 a.m. two centres of low pressure were over the lower St. Lawrence and central Quebec. Rain fell steadily during the morning, so much so that the insulation failed, and during the afternoon the weather cleared—typical of conditions after the passage of a front. On the morning of the 23rd the sky was still overcast and rain flurries

continued throughout the day with very little wind. The potential gradient disturbance cleared about midnight on the 22nd, but minor disturbances appeared during the 23rd probably owing to rain flurries. The weather map for the 23rd showed a large anticyclone over the central United States which

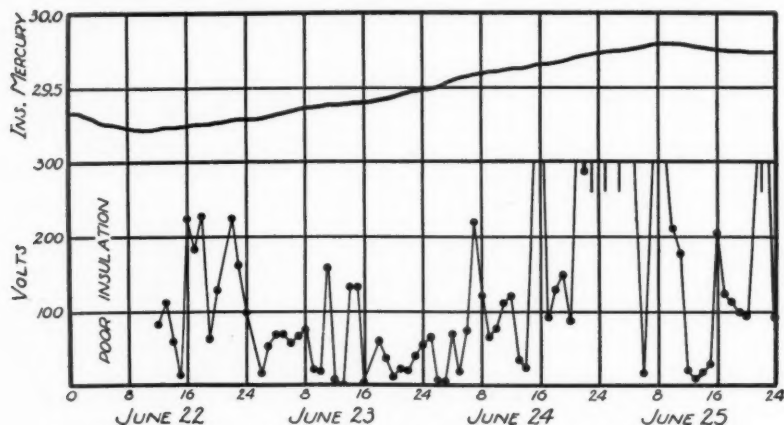


FIG. 11. Potential gradient disturbances, June 22-25, 1935, laboratory station.

was gradually spreading over the eastern half of the continent, as was shown by the slow rise in the barometer. The sky was still partly overcast with cumulus clouds on the 24th but the visibility was excellent. The potential gradient became disturbed on the 24th sometime before the maximum in the barometer was reached. This again was probably due to the fact that the movement of air was from the southwest and the effect of pollution from the city would be expected.

Conclusions

In summary of the results obtained at the country station it is apparent that practically every potential gradient disturbance of any magnitude may be traced to local meteorological conditions. The time at which a potential gradient disturbance starts or stops with respect to the time of passage of a cold front varies so much that no definite rule can be made about it. Usually the potential gradient becomes disturbed several hours before the passage of the front and the disturbance lasts until several hours after the front has passed. Major disturbances in the potential gradient, as would be expected, occur during rain and thunderstorms, but disturbed periods are by no means limited to the times of precipitation. Disturbances when no rain falls do not appear to be as violent as those during rain, but as data giving the times during which precipitation fell at the station are lacking no definite conclusions in regard to this point can be drawn. Apart from times of precipitation the disturbances are due to changes in the ionic equilibrium caused by increased turbulence at a front, or by charges developed in clouds which have not developed into thunderstorm, or are due perhaps to nearby thunder

clouds. Whether electric charges may develop in clouds from which precipitation is not falling is uncertain. Sil (17) finds that the potential gradient is disturbed when cumulus or alto-cumulus clouds are forming overhead. If electric charges are formed in such clouds which have not developed to such an extent that drops of water of appreciable size are formed, some new theory of the production of electric charges in thunderstorms other than Wilson's theory (21), which involves the motion of drops of water, is required.

The duration and magnitude of the potential gradient disturbance appear to depend on the slope of the frontal surface, the strength of the front, and whether a centre of low pressure passed near by. There is probably at least a quantitative relation between the magnitude of the potential gradient disturbance, the duration of the disturbance, and the strength of the front. In the summer months, winds as a rule are lighter and the barometer variation is smaller than in autumn and winter periods. A corresponding difference in the potential gradients would be expected. The period during which the station was operated (four months) is hardly long enough to give much information on this point, but the potential gradient disturbances do appear to be off the scale oftener and for longer periods in the autumn months than in the summer. That the total disturbed time is greater in the autumn than in the summer is shown by the figures in Column 6 of Table I, the part referring to the country station. The corresponding figures obtained at the laboratory station, because of its geographic relation to the city, represent more the percentage of winds in the northwest quadrant than the effect of the passage of fronts.

To study quantitatively the relation of potential gradient to the passage of fronts the following data are noted. Dividing the four months during which the country station was operated into periods between the passage of anticyclones of sufficient strength to produce an undisturbed potential gradient for a day or more, one finds:

Twenty-six cases where the potential gradient disturbance coincides with the passage of a front or fronts in the general way outlined above.

Nine cases where information is incomplete owing to unsatisfactory operation of the apparatus or incomplete meteorological information, but agreement appears likely if information were complete.

Three cases where there was no clear relation between potential gradient disturbances and fronts. In two of these the front was so weak that no appreciable barometer variation was noted. In the third case a definite front passed with no potential gradient variation.

Four cases where a disturbance occurred at the centre of an anticyclone as noted in the description of Figs. 5 and 7.

While this work was in progress, Schou (15) reported some work in which negative conductivity and potential gradient were studied in relation to the passage of fronts. Considerable emphasis was laid on the discontinuity in negative conductivity at the passage of the fronts, but no study was made of disturbances in potential gradient at such periods. Cooper (6) has inter-

puted measurements of potential gradient disturbances spread over a number of years to indicate a correlation between the passage of sun spots and disturbances in potential gradient. In the case of the present observations the disturbed periods coincided so well with meteorological conditions that it seemed unnecessary to look for such an improbable effect.

In conclusion, there is one other effect which is interesting in that it confirms the explanation, given by the author, of the differences between the effects found at the country and laboratory stations. If one averages the deviations from the mean values over periods of say 12 hr. and plots these on a polar diagram, the basis for which is wind direction, the diagram shown in Fig. 12 is the result. The average is taken for 12-hr. periods from 1 to 12 hours

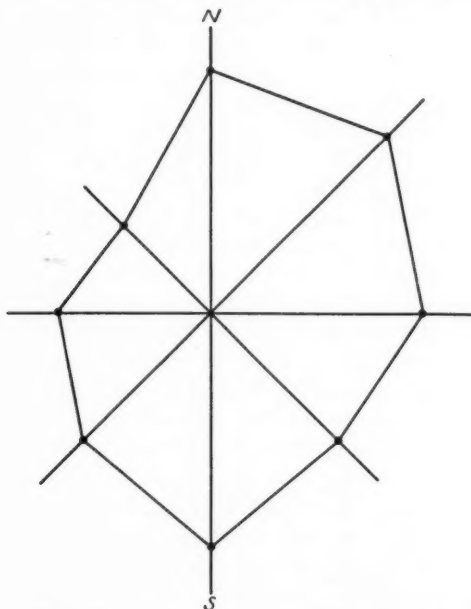


FIG. 12. Mean deviation plotted against wind direction.

each day that the laboratory station was operated. Where the electrometer fibre is off the scale the deviation used in averaging is arbitrarily taken as 350 volts. These are divided into eight groups in accordance with the wind directions given on the 8 a.m. daily weather maps. The average deviation is then found for each group.

Now consider the minimum deviation, *i.e.*, when the wind is northwest. Take this to represent the magnitude of potential gradient disturbances under most stable conditions and subtract it from the value when the wind is in other directions. A figure shown by the full lines in Fig. 13 is obtained. The broken curve represents a rough estimate of the population density in the cities of

Ottawa and Hull plotted with respect to direction from the laboratory. The estimate is made merely by measuring to the outskirts of the region covered by the cities on a large scale map of the surrounding area, park and uninhabited areas being omitted. The measurements are plotted to a scale which makes the two curves fit at one point. The similarity between the two curves in the W,SW,S, and SE directions, and the differences in the N,NE, and E

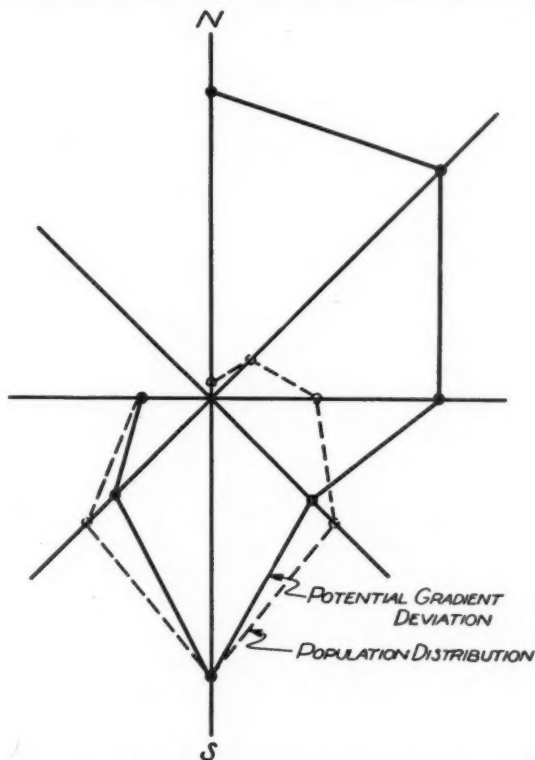


FIG. 13. Potential gradient disturbances plotted against direction of wind compared with population distribution.

directions are apparent. The explanation lies in the geographic relation of the laboratory and the prevailing direction of winds in fine and stormy weather. Where the shape of the potential gradient deviation curve is similar to the population distribution curve, the potential gradient disturbance can be blamed on city pollution. When stormy weather typical of an approaching front with a nearby depression is approaching, the wind is usually in the north to east quadrant. The value of the point representing disturbances from the north may be enhanced somewhat by the presence of the laboratory heating plant. Similar curves for the four seasons show slightly different shapes.

Acknowledgments

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WATER SOLUBLE ACID SUBSTANCES IN THE RAW HUMUS OF PODSOL SOILS¹

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Abstract

Aqueous extracts of "raw humus" from a typical Quebec podsol soil have been studied by means of two methods of fractionation. The presence of free acetic acid and mannitol has been established, and evidence of the presence of formic acid has been obtained. Data are presented which show that a number of organic acids are present in small quantities.

The most prevalent virgin soil type found in the province of Quebec is the podsol. Surface waters percolating through the soil have removed soluble bases from the upper soil horizons and brought about a deposition of sesquioxide-organic complexes at lower levels. A knowledge of the causes of this leaching process may suggest means of increasing the fertility of podsolized soils.

Laboratory experiments have shown that aqueous extracts of the surface layer of decaying organic matter are strongly acid in reaction and exert a leaching effect on the subsoil. An examination of these extracts was undertaken to determine the nature of the substances present. Particular attention was given to acid substances since they are known to cause leaching of soil minerals (5).

Though much attention has been given to the hydrogen ion concentration of soils, little information has been obtained regarding the nature of the acids present. The mineral acids, sulphuric and phosphoric, are considered by some workers (1) to be responsible for soil acidity, but this hypothesis has not been proved. Schreiner and Shorey (8, 9, 10) and Shorey (11, 12) have isolated a number of organic acids from soils. However, the methods used for the isolations and the nature of the soils investigated make it appear highly improbable that these acids occurred in the free state.

The material used for the present investigation was "raw humus" from a typical sandy podsol near Ste. Anne de Bellevue, Quebec. The humus was obtained from an almost pure stand of hemlock (*Tsuga canadensis*), was

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strongly acid in reaction, and contained 16 to 20% of ash. Extracts were prepared and subjected to an examination by two methods, one based on precipitation with barium hydroxide and the other on a preliminary fractionation with organic solvents.

Two organic substances were isolated from the extracts. Mannitol was obtained in amounts representing 3 to 4% of the dissolved organic matter. The baryta method yielded acetic acid in an amount equivalent to about 8% of the total acidity, and evidence was obtained of the presence of formic acid in about one-fourth of this amount. The method of solvent fractionation also gave evidence of the presence of volatile acids in an equivalent amount, and since in this case the acids were distilled under reduced pressure directly from the extracts it is concluded that they were present in the free state.

As far as the authors are aware, the presence of free acetic and formic acids in soils of this type has not been reported previously. Mannitol was found in soil by Shorey (11). Raistrick and co-workers (2) found it as an intermediate product in the action of molds on glucose. While the source of the mannitol is not definitely known, its presence appears significant because polyhydroxy compounds form complexes with trivalent bases.

Experimental

Preparation of Soil Extracts

The humus was screened and saturated with distilled water in four-litre percolators holding 700 grams of humus each, allowed to stand for 20 hr., drained, and washed with 0.5 litres of water, and the process repeated once. The extracts varied slightly in composition but the following data are typical. From 1000 gm. of anhydrous humus 4.3 litres of extract, containing 3.5 gm. of dry matter, was collected. The pH of the solution was 3.3, and the total acidity was equivalent to about 5.2 ml. of normal acid.

The extracts were colored and highly buffered. Consequently the acid values were determined electrometrically by means of a hydrogen electrode. Titration curves were drawn and the equivalence point was taken as pH 7.0.

Fractionation by Means of Barium Salts

The filtered extract was treated with a slight excess of saturated barium hydroxide solution. A dark brown precipitate containing the insoluble barium salts was filtered off and washed with hot water. This precipitate was treated with the calculated amount of sulphuric acid, and the liberated acids were divided into water soluble and water insoluble fractions. The insoluble acids were separated from barium sulphate with sodium carbonate. The distribution of the acidity for these fractions is given in Table I. The combined filtrate and washings containing the soluble barium salts were treated with carbon dioxide and concentrated at 80° C. The acids were liberated with sulphuric acid and distilled. Data for the acidity of the volatile and non-volatile fractions are given in Table I.

TABLE I

DISTRIBUTION OF ACIDITY IN EXTRACTS BY THE BARYTA METHOD OF FRACTIONATION

Fraction	0.1 N acid per kg. of humus, ml.	Total acidity, %
Barium salts insoluble in water		
Acids soluble in water	22.0	29.4
Acids insoluble in water	1.9	2.5
Barium salts soluble in water		
Volatile acids	12.8	17.1
Non-volatile acids	29.0	38.6
Recovery	65.7	87.6

A quantity of the distillate equivalent to 30 kg. of humus was made slightly alkaline and concentrated to a volume of 10 ml. After acidification with sulphuric acid the solution was extracted with ether. Two fractionations of the ethereal solution yielded 2 ml. of a fraction boiling at 100° to 110° C., which exhibited a reducing effect on Tollens' solution. Formic acid was determined in one-half of this fraction by a modification of Scala's method (4, 7, 13), in which the mercurous chloride was weighed. Found: HCOOH, 0.012 gm. per kg. of raw humus, which is equivalent to 21% of the volatile acidity.

The remainder of this fraction was treated with *p*-phenylphenacyl bromide (3) and after two recrystallizations the resulting ester was found to have a melting point of 109° C. No depression of the melting point occurred when this ester was mixed with an authentic specimen of *p*-phenylphenacyl acetate, m.p. 110° C. About one-fifth of the volatile acidity is, therefore, due to formic acid, and the remainder largely to acetic acid.

The residue that remained after removal of the volatile fraction was dissolved in a minimum quantity of water, treated with five volumes of 95% ethyl alcohol, and filtered to remove precipitated gums. The filtrate, when treated with two-thirds its volume of ether, yielded mannitol. The mannitol was recrystallized from alcohol and its identity was confirmed by the melting point when admixed with an authentic specimen.

This fraction contained, besides mannitol, a mixture of distinctly acid substances which were neither colloidal nor resinous, but all attempts to isolate individual acids were unsuccessful.

Fractionation by Means of Solvents

After a number of preliminary investigations the scheme of fractionation outlined in Fig. 1 was developed. Analyses of the various fractions are given in Table II.

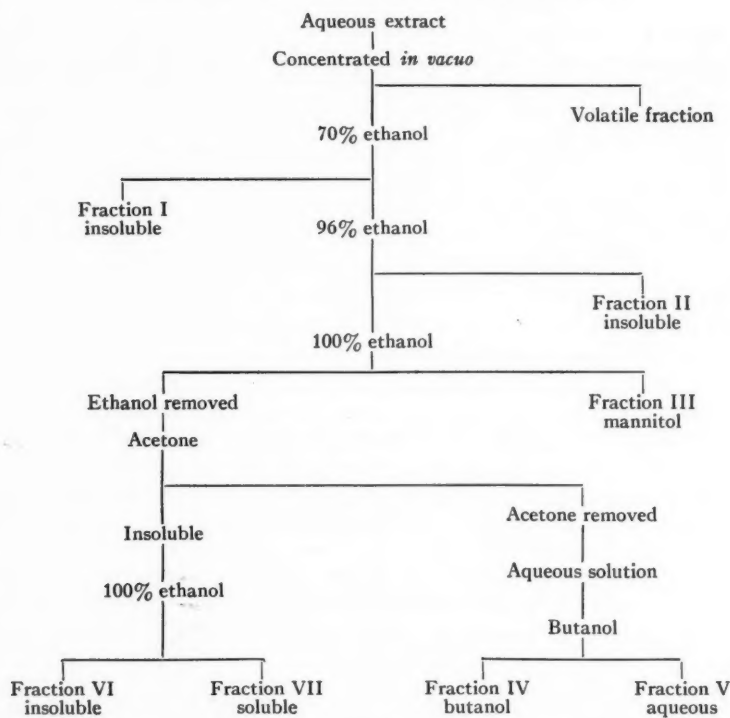


FIG. 1. Fractionation of humus extracts by means of solvents.

TABLE II

ANALYSES OF FRACTIONS OBTAINED FROM HUMUS EXTRACTS BY MEANS OF SOLVENTS

Fraction	Relative leaching power*	Solids, %	Acidity, %	Acid equivalent	Nitrogen, %	Sulphur, %	Phosphorus, %
Volatile	38	1.1	11.5	60	0.0	0.0	0.0
Insoluble in ethanol							
I. 70%	—	26.6	24.0	780	3.2	6.3	0.3
II. 96%	131	26.1	10.6	1650			
Soluble in acetone							
IV. Sol. butanol	166	8.9	25.9	230	0.0	0.0	0.0
V. Sol. water	389	3.1	8.6	245	0.0	0.0	0.0
Insoluble in acetone							
VI. Insol. ethanol	—	3.4	0.0	0.0	—	—	—
VII. Sol. ethanol	194	4.3	13.8	208	2.4	2.7	0.01

* Milligrams of iron removed from 2.0 gm. of soil by 0.5 gm. of each fraction in 100 ml. of water.

In a typical experiment, the filtered extract from 25 kg. of anhydrous raw humus (94 litres, containing 76.2 gm. of dissolved solids) was concentrated to two litres, in an atmosphere of nitrogen, under reduced pressure below 40° C., and filtered. The filtrate was poured in a fine stream, with agitation, into seven litres of 95% ethanol; thus the concentration of the ethanol was reduced to 70%. The precipitate was washed first with 70% ethanol, then with 95% ethanol and dried over sulphuric acid and solid sodium hydroxide under reduced pressure. It was a brown powder weighing 20.3 gm. (26.6% of the total dissolved solids). The filtrate and washings, concentrated to 100 ml. and poured into absolute ethanol to a final concentration of 97%, yielded a further precipitate of 21.5 gm. (28.2% of the dissolved solids.) In a similar experiment in which 17 kg. of raw humus was used the two alcohol precipitated products amounted, respectively, to 26.5 and 23.9% of the dissolved solids.

The red alcoholic filtrate, concentrated to less than 100 ml. and treated with additional absolute ethanol, deposited crystals, which, after recrystallization from 90% ethanol, were identified as mannitol by the method of mixed melting points and also by the preparation of the hexacetate, m.p. 120° C. The quantity isolated constituted 3 to 4% of the total organic matter of the soil extract.

The volatile acids were collected during concentration of the extracts. Qualitative tests indicated the presence of acetic acid, but attempts to prepare the *p*-phenylphenacyl ester yielded a mixture of derivatives which could not be separated by fractional crystallization.

Fraction IV was dissolved in dry methanol and treated at 2° C. with 9.0 gm. of diazomethane generated by the method of Meerwein and Burneleit (6). The esters were extracted from an aqueous medium with ether, freed from acid material with 2.5% potassium carbonate solution and fractionally distilled. The following fractions were obtained.

- (a) B.p. 40° to 50° C. at 25 mm. 0.12 gm. of colorless mobile liquid. Redistilled, b.p. 89° to 89.5° C. at 760 mm., 0.08 gm.
- (b) B.p. 60° to 65° C. at 0.5 to 0.6 mm., 0.15 gm. of yellow oil.
- (c) B.p. 97° to 100° C. at 0.1 mm., 0.20 gm. of yellow oil.
- (d) B.p. 140° to 160° C. at 0.04 mm., 0.40 gm. of resinous yellow oil. Redistilled, b.p. 120° to 122° C. at 0.03 mm., 0.30 gm. of yellow oil with tendency to crystallize on standing.

The esters were obtained in quantities too small for identification. The *p*-phenylphenacyl ester was prepared from Fraction (a), and it melted at 120° C. A search of the literature failed to identify this derivative.

Fraction VII was dissolved in water and an aliquot was treated with barium hydroxide. A colloidal precipitate formed which was free from sulphur and was completely soluble in dilute hydrochloric acid. It is, therefore, evident that the acidity of this fraction was not due to sulphuric acid. Picric acid

yielded a mixture of crystalline picrates which could not be separated, owing to the small quantity of material available and the presence of colloidal impurities. The excess picric acid was removed and the solution treated with phosphotungstic acid. A white precipitate containing sulphur but no nitrogen was obtained. As the picrates were sulphur-free and contained all the nitrogen of the extract, a complete separation of sulphur and nitrogen had been realized.

Acknowledgments

The authors are greatly indebted to Dr. J. F. Snell for his unfailing interest in this investigation, and his co-operation in the preparation of the manuscript; and to Dr. P. H. H. Gray for helpful criticism.

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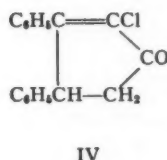
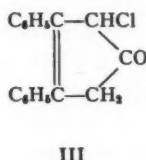
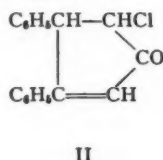
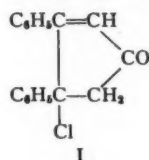
THE 3,4-DIPHENYLCHLOROCYCLOPENTENONES AND RELATED COMPOUNDS¹

BY C. F. H. ALLEN² AND H. RUDOFF³

Abstract

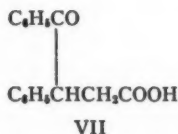
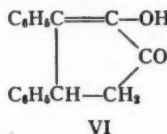
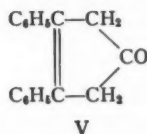
The uncertainties as to structures in the 3, 4-diphenylchlorocyclopentenones have been cleared up by the synthesis of all four possible isomers and a study of their reactions. The investigation of the related indones has been continued, and an interpretation of new evidence is suggested.

In order to clear up the uncertainties as to the location of the double bond and of the chlorine atom in the diphenylcyclopentenone series, the earlier work (3) has been extended and evidence secured which makes it possible to assign definite structures to each form. The four possible isomers are represented by Formulas I to IV.



A substance corresponding to I was first made and its structure determined in this laboratory (3); this formula was confirmed and accepted by other workers in the field (7). At the same time (3) the arrangement shown in II was assigned to an isomeric chloride, first obtained 50 years ago by Japp (12), because both gave the same indone by loss of hydrogen chloride on treatment with alkaline reagents. This structure, however, was not accepted by the English investigators (7) who preferred to represent it as IV for reasons that seemed best to them. They also synthesized a third chloride, to which was assigned Formula III, and with which the writers are in agreement.

To complete the series and end the confusion, the writers have synthesized the fourth possible isomer; so now all are known and it remains only to assign structures to the new one and to Japp's. All four contain the cyclopentenone system, for each can be converted into the diphenylcyclopentenone V. Each gives a different dinitrophenylhydrazone when treated with 2,4-dinitrophenylhydrazine. This not only serves as a means of identification but also shows that each contains a carbonyl group.



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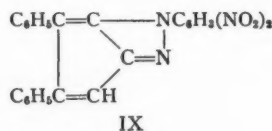
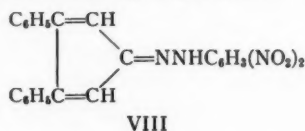
³ Graduate Student, McGill University, and holder of a bursary (1935-1936) under the National Research Council of Canada.

The fourth chloride was prepared by the action of phosphoryl or sulphuryl chloride on Vorländer's ketol, VI. This type of reaction was employed by Emil Fischer in his work with the purines, to replace the hydroxyl group on a doubly bound carbon by a chlorine atom (11). When the new chloride was ozonized a 60% yield of desylacetic acid, VII, resulted; thus the double bond was located. This reaction, taken in conjunction with the method of preparation, and the inactivity of the chlorine, makes certain Structure IV for the new isomer. By exclusion, therefore, Japp's isomer must be represented by II as the writers formerly postulated, though the reason given at that time is no longer valid.*

The conversion of chloride I to II, described in the earlier paper, is, as the English investigators suggested, a case of anionotropy, for it is brought about by hydrogen chloride or hydrogen bromide in acetic acid; if it were elimination and addition, a bromide should have resulted in the second case. The sequence of shifts, *i.e.*, whether chlorine or hydrogen migrates first, is uncertain; a prior movement of chlorine would give III, but since attempts to rearrange III to II in the same way were unsuccessful, such an assumption seems unwarranted.

The difference in reactivity of the chlorine atom in these compounds makes it possible to put them into two groups. The first, which give immediate precipitates with silver nitrate, contains I and III, the chlorine of the former resembling that of a tertiary chloride such as triphenylchloromethane, while both are like allyl chloride. The second group contains II and IV; the chlorine atom is relatively inactive and gives no precipitate with silver nitrate.

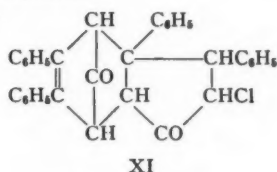
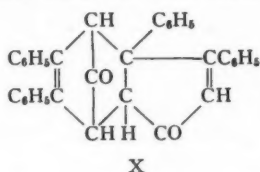
Though each chloride gives a dinitrophenylhydrazone, the derivative from III has lost its chlorine; it is monomolecular and believed to be the dinitrophenylhydrazone of diphenylcyclopentadienone, VIII. It could not be split into its components; all the variations ever reported (1) for cleavage of dinitrophenylhydrazones were tried, but the derivative was recovered unchanged. An alternative, Formula IX, containing a four-membered ring is possible but extremely improbable.



All the chlorides react with basic reagents, but the products are not always well defined. Chloride I loses hydrogen chloride the most easily, any basic reagent (even silver nitrate) causing the formation of the indone X (3). The latter is also secured from II but only by the use of a strong base such as sodium hydroxide. Isomer III gives with sodium hydroxide a monochlorin-

*Burton, Shoppee and Wilson (7) obtained some desylacetic acid by the permanganate oxidation of Japp's chloride. This led them to advocate IV for this substance; ozonolysis yielded an oil. Since the use of alkaline reagents, such as permanganate, is not trustworthy in $\alpha, \beta - \beta, \gamma$ -unsaturated systems in which shifts of hydrogen and double bonds are possible, this reaction cannot be considered reliable for proving structure.

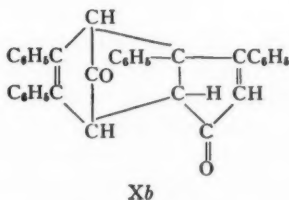
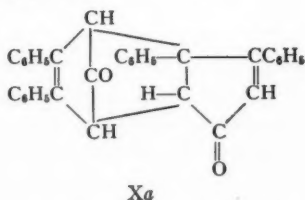
done XI, which on boiling with sodium methylate loses hydrogen chloride to give X. It is thus to be represented as a hydrogen chloride addition product of X rather than as a substitution product which the English investigators suggested, based on their method of preparation.



Chloride IV likewise loses hydrogen chloride, when sodium carbonate and dilute alcohol are used; the product is bimolecular, but its exact nature is undetermined. Since it loses carbon monoxide on heating, it contains a carbonyl bridge (2); the analysis shows that it contains a molecule of chemically combined alcohol which cannot be removed by acetic anhydride. It is probably the methoxyindone corresponding to XI.

The mechanism of formation of the indone X has already been considered (3). That of the chlorindone probably starts in the same way, with formation of the cyclopentadienone, which at once adds a second molecule of the chloride to form XI. The evidence is insufficient for further theorizing.

To learn more about substances such as the indone X, of which very few examples are known, it was treated with chromic acid, and an isomer was obtained. This isomer, when heated above its melting point, lost carbon monoxide. Hence, it contained a carbonyl bridge (2); this excluded any of the possible open chain formulas. It reverted to the starting material when treated with mineral acids, or spontaneously on long standing. This behavior led to the conclusion that the starting material was a mixture of two substances, one of which was oxidized by the chromic acid so much more rapidly than the other that the second could be isolated. The idea that it was a mixture was encouraged by the observation that the melting points of different preparations varied over a small range, though no other way of separation was found. An inspection of X reveals that geometrical isomerism of the decalone type is possible.

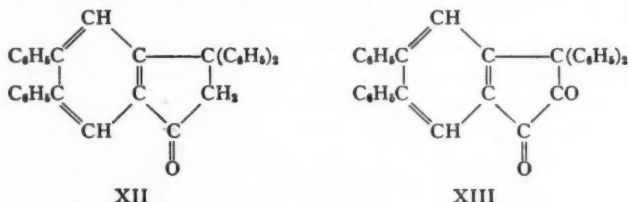


In the hydrindene series, to which these substances may be considered to belong, Hückel and others have shown that it is impossible to state with any degree of certainty whether the *cis* or *trans* form would be expected to be

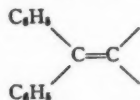
more stable. Further, in the decalone series the *cis* is easily changed into the *trans*, presumably through enolization. In the case at hand, if it be assumed that the two forms are in a fairly mobile equilibrium, the changes described above are readily accounted for.

The problem of deciding which is *cis* is even less satisfactorily answered. Based on the observation that one form loses carbon monoxide on heating to give an unstable substance which then adds maleic anhydride (3), and upon an examination of space models of the second substance, of which only the *cis* form could add maleic anhydride without distortion, the *cis* arrangement **Xa** is tentatively suggested for that isomer. The *trans* linking **Xb** is thus left for the more stable form obtained after the chromic acid treatment.

The difference between the two is also shown by an examination of the results of pyrolysis. The new (*trans*) isomer gives an entirely different kind of substance, to which has been assigned Structure **XII**, although the evidence is not as complete as could be desired. The evidence is as follows:—



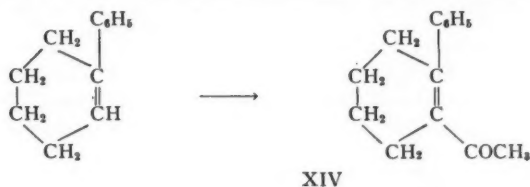
selenium dioxide gives a red diketone **XIII**, which is reduced back to the original substance by zinc and acetic acid. There are two hydrogen atoms which can be replaced by bromine or chlorine; the halogen is removed by reduction to give the starting material. It shows one addition in the Grignard machine, but does not give an oxime. It could be formed by the enolization of **X**, with the hydrogen atom returning to a carbon atom different from the one to which it was originally attached, with a concomitant 1,2 shift of a phenyl group. The necessary conditions of electromeric shift of the double bond possibly relate this to the corresponding rearrangement of tolane to



The diketone could not be degraded to a known substance. It showed addition of two molecules of methylmagnesium iodide in the Grignard machine. It formed a monoxime. It reacted with *o*-phenylenediamine, but from the analytical figures the product is an anil, rather than a quinoxaline; the presence of the two phenyl groups doubtless hinders the activity of the adjacent carbonyl so that it is relatively inactive. Sodium peroxide reacted but slowly and the product seemed unrelated to the starting material. None of the substances added maleic anhydride.

The behavior of the mixture on pyrolysis may be explained in this way—the *cis* (lower melting) form loses carbon monoxide at the melting point; this removes it from the equilibrium mixture. The *trans* isomer rearranges below the temperature at which it loses carbon monoxide, so that the mixture acts as a single substance and gives but one product.

Attempts* made to prepare some simpler 9-phenyldecalins have been unsuccessful. When Ruzicka's procedure (13) for the 9-alkyldecalins, which started with 1-methylcyclohexene, was adapted by substituting 1-phenylcyclohexene, it was impossible to get beyond the formation of the unsaturated ketone XIV; not even cyanoacetamide could be added to the latter.



2,3-Dimethylbutadiene added to 2,5-diphenylquinone by Fieser's reaction (9, 10), but the untractable products did not have any of the expected properties.

Experimental

I. WORK ON CHLORIDE IV; 3,4-DIPHENYL-2-CHLOROCYCLOPENTEN-2-ONE-1

A mixture of 5 gm. of Vorländer's ketol (15) and 15 cc. of phosphoryl chloride was refluxed for 15 min., during which time the solid dissolved. The dark, cooled reaction mixture was added to 100 gm. of cracked ice, and the oil that separated was left to crystallize. It was dissolved in a minimum amount of hot alcohol and decolorized with Nuchar. After two treatments it formed pale yellow flakes, m.p. 142° C.†; the yield was 1.5 gm. (29%). It was very soluble in the usual solvents. Calcd. for $C_{17}H_{13}OCl$: Cl, 13.2%. Found: Cl, 13.2%.

A better quality of product was secured by the use of sulphuryl chloride, but most of the ketol was unattacked.

(1) The dinitrophenylhydrazone, prepared by Brady's procedure (5), separated in carmine needles from a 1:1 chloroform-methanol mixture; m.p. 216–217° C. Calcd. for $C_{23}H_{17}O_4N_4Cl$: N, 12.5%. Found: N, 12.5%.

(2) Reduction: 3,4-diphenylcyclopentanone. One gram of the chloride was refluxed with 2 cc. of 48% hydriodic acid and 0.6 gm. of red phosphorus in 5 cc. of acetic acid for four hours, filtered hot, and the solution was poured into 70 cc. of water containing a little sodium bisulphite. The oil that separated was extracted with ether, and after appropriate manipulations, including a treatment with Nuchar, was poured into an equal volume of acetone. The

*Work of Dr. L. F. Halley.

†Melting points are corrected.

solid (or oil) was separated and crystallized with difficulty (because of its great solubility in everything except water in which it dissolves to some extent) from a 2:1 water-alcohol mixture. It separated in white needles, m.p. 92°C ., and did not decolorize bromine. The same substance was secured in a less pure condition by a similar reduction of Vorländer's ketol. The dinitrophenylhydrazone, prepared as outlined above, formed dark red, iridescent needles, m.p. 228°C . Calcd. for $\text{C}_{23}\text{H}_{20}\text{O}_4\text{N}_4$: N, 13.5%. Found: N, 13.4%.

(a) Dehydrogenation of 3,4-diphenylcyclopentanone to 3,4-diphenylcyclopenten-3-one. On refluxing 0.2 gm. of the saturated ketone with 0.15 gm. of selenium dioxide in 10 cc. of dioxane for two hours, and working up, an oil was obtained which was immediately transformed into the dinitrophenylhydrazone. The latter, m.p. 233°C ., was identical with the derivative prepared directly from the unsaturated ketone; the mixed melting point was not depressed. This reaction was repeated, always with the same result.

(b) 3,4-Diphenylcyclopenten-3-one and Vorländer's ketol gave 2,4-dinitrophenylhydrazones by Brady's procedure. The first formed red prisms, m.p. 233°C ., while the latter separated in purplish-red needles, sintering above 230°C . and melting at 239° to 240°C . Calcd. for (a) $\text{C}_{23}\text{H}_{18}\text{O}_4\text{N}_4$: N, 13.5; (b) $\text{C}_{23}\text{H}_{18}\text{O}_5\text{N}_4$: N, 13.0%. Found: (a) 13.5; (b) 13.2%.

(3) Ozonolysis of the chloride. The chloride (0.1 gm.) in 50 cc. of pure ethyl acetate was treated with ozonized oxygen (12% ozone) for 70 min. The solvent was removed *in vacuo*; this left a gummy residue which deflagrated on heating. The ozonide was decomposed by water containing a little hydrogen peroxide and a few crystals of ferrous sulphate, the oil extracted with ether, dried, and added to an equal volume of acetone. On spontaneous evaporation, desylacetic acid was deposited, and was identified by its melting point (161° to 162°C .) and by the mixed melting point obtained with an authentic specimen.

Potassium permanganate destroyed the chloride, giving benzoic acid and a tar, but dilute chromic acid was almost without action.

(4) Action of basic reagents on the chloride. The latter was unaffected by silver nitrate, potassium acetate, and pyridine, but the chlorine was removed by piperidine, sodium carbonate, and sodium hydroxide. A suspension of 1.6 gm. of the chloride, 50 cc. of methanol, and 5 gm. of sodium carbonate was refluxed on the steam bath for a half-hour, and filtered. On standing, 1.1 gm. (70%) of white prisms, m.p. 208°C . after recrystallization from methanol-acetone, was obtained. It evolved carbon monoxide rapidly at 250°C . Calcd. for $\text{C}_{35}\text{H}_{28}\text{O}_3$: C, 84.7; H, 5.7; OCH_3 , 6.2%; mol. wt., 496. Found: C, 84.7, 84.3; H, 5.7, 5.5; OCH_3 , 6.0, 6.0%; mol. wt., 501.

This substance was unaffected by acetyl chloride, acetic anhydride, or hydrogen chloride in acetic acid. It did not give an oxime, but showed 1.2 active hydrogen in the Grignard machine.

II. WORK WITH CHLORIDES I AND II

(1) Rearrangement of I into II (Japp's) by hydrogen bromide. The procedure was the same as that previously described (3), in which hydrogen chloride in acetic acid was used. After four days, chloride II (m.p. 128° C.) and indone X were separated and identified by mixed melting points.

(2) The dinitrophenylhydrazones of I and II were prepared as outlined above; both separated in red needles from methanol-chloroform, with the same melting point, 216° C. Mixed melting points of all the dinitrophenylhydrazones were depressed 20° C. The derivative of I was unaffected by refluxing with alcoholic potassium acetate; the others were not submitted to this treatment. Calcd. for $C_{23}H_{17}O_4N_4Cl$: N, 12.5%. Found: N, (I) 12.6; (II) 12.5%.

(3) When 0.5 gm. of chloride I in acetone was treated with 0.4 gm. of powdered potassium permanganate and 0.3 gm. of magnesium sulphate for 24 hr., and worked up, 0.3 gm. of the indone X was isolated from the acetone extract.

(4) When the same chloride was warmed with 5% alcoholic silver nitrate, an abundant precipitate of silver chloride had formed after two minutes; the indone was isolated from the solution. Piperidine likewise gave the same substance.

When chloride II was refluxed for 1.5 hr. with 5% silver nitrate there was no action, the starting material being recovered unchanged. Piperidine hydrochloride was isolated after a treatment with this base, but no other crystalline material was found.* It was unaffected by ozone in ethyl acetate after 1.5 hr.

III. WORK ON CHLORIDE III

(a) The 2,4-dinitrophenylhydrazone was prepared in the same manner as the others; it separated in red needles, m.p. 265° C. with decomposition. It did not contain chlorine. Calcd. for $C_{23}H_{16}O_4N_4$: N, 13.6%; mol. wt., 412. Found: N, 13.7, 13.8%; mol. wt., 435. It was unattacked after treatment with sodium pyruvate, picryl chloride or by sodium carbonate and methanol, by heating in a sealed tube with acetone or acetaldehyde, but was destroyed by alcoholic potash.

(b) A precipitate of silver chloride was formed immediately on the addition of alcoholic silver nitrate to a similar solution of the chloride; no crystalline material could be isolated from the filtrate.

(c) The chlorindone XI separated on refluxing for four hours a mixture of 1 gm. of the chloride, 5 cc. of methanol, and 30 cc. of 5% aqueous sodium hydroxide; it crystallized in thin prisms from methanol-acetone; m.p. 204° C. with evolution of carbon monoxide.

When 5 mg. was refluxed in 1 cc. of dilute sodium methylate for several hours and allowed to stand, 3 mg. of the indone X slowly crystallized.

*The indone gives a viscous product when boiled for any length of time with alcoholic potash; this explains why the English authors (7) did not repeat our work (3). We have had no difficulty, but avoided long heating.

IV. PREPARATION AND REACTIONS OF THE INDONE Xb

1. *Action of Chromic Acid on the Indone X*

Five grams of the indone X, as obtained by the dehydration of anhydrazetonebenzil, was dissolved in 25 cc. of boiling acetic acid, and a solution of 4 gm. of chromic trioxide in 20 to 30 cc. of hot acetic acid was slowly added through the condenser. When all the reagent had been added, the mixture was boiled for 15 min., and allowed to stand overnight, when 2.5 gm. of white needles was deposited; these were filtered and recrystallized from a minimum quantity of amyl ether or from a 1:1 chloroform-methanol mixture. The melting point was 264° C. with evolution of gas. The substance showed one active hydrogen and one addition in the Grignard machine. Calcd. for $C_{34}H_{24}O_2$: C, 87.9; H, 5.2%; mol. wt., 464. Found: C, 87.3, 87.3; H, 5.4, 5.5%; mol. wt., 434.

The new substance was unaffected by maleic anhydride, and by four hours' refluxing with aqueous or alcoholic solutions of sodium hydroxide up to 30% strength. It did not form an acetal.

When it was refluxed with 25 cc. of acetyl chloride for one-half hour, and the red-brown solution allowed to cool, 4.5 gm. of white stubby prisms was deposited, m.p. 206° C., with evolution of gas. A mixed melting point with X showed no depression. Passage of dry hydrogen chloride through an acetic acid solution of X gave the same result.

(2) *Pyrolysis of Xb; Formation of 3,3,5,6-Tetraphenylhydrindone, XII*

Five grams of the substance was melted (265° to 270° C.) in a metal bath. After the evolution of gas had ceased, the light brown liquid was allowed to cool; it solidified to a glass. This was crystallized from 1:1 chloroform-methanol, as white needles, m.p. 182° C. The average yield was 85%. The product was soluble in chloroform, acetone, benzene, warm acetic acid; sparingly soluble in ethanol, and almost insoluble in methanol; it did not dissolve in dilute acid or alkali. In the Grignard machine it showed one addition. It did not add maleic anhydride. Calcd. for $C_{33}H_{24}O$: C, 90.8; H, 5.5%; mol. wt., 436. Found: C, 90.9; H, 5.6%; mol. wt., 453.

(a) *Reactions of XII*

(i) *Bromination.* One gram of the substance was dissolved in 15 cc. of acetic acid and a few bubbles of hydrogen bromide were passed through the solution; 1 cc. of bromine was then added and the mixture refluxed for 15 to 20 min., during which time hydrogen bromide was evolved. The white needles that were deposited were recrystallized from a methanol-chloroform mixture. The yield was 0.65 gm., m.p., 265° C. Calcd. for $C_{33}H_{22}OBr_2$: Br, 26.9%. Found: Br, 27.0%.

(ii) *Chlorination.* One gram of the compound was dissolved in 6 cc. of cold sulphuryl chloride. After standing for 15 min. the solution was cautiously poured into water and the mixture extracted with chloroform; the chloroform extract was dried over calcium chloride, and on slow evaporation deposited

a white solid which separated from acetic acid in white needles, m.p. 252° C. Calcd. for $C_{33}H_{23}OCl_2$: Cl, 14.1%; mol. wt., 505. Found: Cl, 14.3%; mol. wt., 504.

Neither halide could be hydrolyzed by boiling with aqueous or alcoholic potassium hydroxide, or with silver acetate.

When 1 gm. of the chloride was refluxed with 1 gm. of mossy zinc in 60 cc. of acetic acid for four hours, the parent compound XII was regenerated in almost quantitative yield. There was no reaction in benzene.

(iii) *Miscellaneous*. It did not form an oxime. It gave tars on fusion with sodium hydroxide or sulphur.

(iv) *Oxidation; Formation of 3,3,5,6-Tetraphenylindandione-1,2, XIII*. A mixture of 2.7 gm. of the ketone, 0.7 gm. of selenium dioxide, and 20 cc. of dioxane was refluxed for six hours with stirring. After filtration from selenium and precipitation by dilution, the red solid was recrystallized from acetic acid; it separated (2.2 gm.) in reddish-orange rods, m.p. 199° to 200° C. It dissolved readily in benzene, acetic acid, and chloroform, but only slightly in the alcohols. It gave two additions in the Grignard machine, but did not add maleic anhydride. Calcd. for $C_{33}H_{23}O_2$: C, 88.0; H, 4.9%. Found: C, 87.9; H, 5.2%.

The oxime, prepared in the usual manner, formed light yellow needles that melted indefinitely at 200° C.; on standing, the needles changed to a powder. A trace of yellow prisms, m.p. 245° C., was also isolated. Calcd. for $C_{33}H_{23}O_2N$ (monoxime; 200° C.): N, 3.0%. Found: N, 2.8, 2.8%.

The solution from 2 gm. of *o*-phenylenediamine hydrochloride and 3 gm. of potassium acetate in 20 cc. of acetic acid was filtered, 1 gm. of the red diketone was added and after 14 min. refluxing the derivative had precipitated. It separated (1.2 gm.) in pale buff prisms, m.p. 272° C., from acetic acid; it is sparingly soluble in methanol, but dissolves readily in chloroform or acetic acid. Calcd. for $C_{39}H_{29}N_2O$: C, 86.7; H, 5.2; N, 5.2%. Found*: C, 86.9; H, 4.9; N, 4.9, 5.0%.

The action of other oxidizing agents, permanganate, chromic acid, or dilute nitric acid was too drastic and destroyed the substance. Sulphuric acid gave no useful product.

Reduction, by refluxing equal weights (1 gm.) of the diketone and zinc dust in 20 cc. of acetic acid for an hour, and the appropriate manipulations, regenerated the indone XII.

Action of sodium peroxide. When 1 gm. of the diketone in 10 cc. of acetone was shaken for four hours with an iced solution of 1.5 gm. of sodium peroxide in 10 cc. of water, 0.5 gm. of white needles was isolated from the acetone layer. Only a trace of solid was secured from the acidified aqueous layer. The needles melted at 257° to 258° C., but were insoluble in aqueous or alcoholic potash up to 50% strength. In the Grignard machine it showed

*The same values were obtained by the Dumas and Kjeldahl methods. The latter would not be expected to give the correct values with a quinoxaline (14).

two replaceable hydrogens but no additions. Found: C, 86.5, 86.5; H, 5.3, 5.6%; mol. wt., 431. With diazomethane it gave a new substance, m.p. 161 to 163° C. Found: C, 91.3; H, 5.9; OCH₃, 7.0, 7.3%.

V. FROM WORK OF DR. L. F. HALLEY. 1-PHENYL-2-ACETYLCYCLO-
HEXENE-1

To a solution of 52 gm. of stannic chloride, 50 cc. of acetyl chloride, and 50 cc. of carbon disulphide, was added, over a period of two hours, 32 gm. of phenylcyclohexene in 50 cc. of carbon disulphide. The temperature of the solution was kept below -35° C. After four more hours the mixture was poured onto ice, the unsaturated ketone isolated by appropriate manipulations, and distilled. A yield of 21.5 gm. (54%) of a product, b.p. 145° to 147° C. at 7 mm., was secured. Calcd. for C₁₄H₁₆O: C, 84.0; H, 8.0%. Found: C, 84.2; H, 8.1%. The 2,4-dinitrophenylhydrazone separated from dilute alcohol in yellow needles, m.p. 165° C. Calcd. for C₂₀H₂₀O₄N₄: N, 14.7%. Found: N, 14.9%.

Reaction between 2,3-dimethylbutadiene and 2,5-diphenylquinone. A mixture of 20 gm. of the quinone, 50 cc. of the hydrocarbon, and 40 cc. of absolute methanol was heated in a sealed tube at 100° C. for five days; 3.6 gm. of a yellow solid was filtered, m.p. 264° to 266° C. From the solution, 16 gm. of a pale yellow glass-like substance, which could not be crystallized, was isolated. When 5 gm. of the latter in 100 cc. of boiling acetic acid was reduced by the gradual addition of 20 gm. of zinc dust, and the organic material precipitated by pouring into water, a solid, m.p. 169° to 170° C., after recrystallization from methanol or acetone, was obtained. Calcd. for C₂₄H₂₄O₂: C, 83.7; H, 7.0%; mol. wt., 344. Found: C, 83.5, 83.6; H, 7.0, 6.9%; mol. wt., 338. Found: (yellow solid) C, 86.9, 86.7; H, 4.4, 4.4%.

The reduced substance evolved hydrogen sulphide but no thiophenol when heated with sulphur, but was so badly charred as to be useless. Various oxidizing and reducing agents gave untractable, amorphous products, plus traces of benzoic acid. The high melting compound was recovered unchanged after two hours' fusion with caustic potash at 400° C.

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THE ACTION OF SATURATED STEAM ON DICALCIUM FERRITE AND ON TETRACALCIUM ALUMINOFERRITE¹

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Abstract

The reactions which occur when dicalcium ferrite and tetracalcium aluminoferrite are exposed to saturated steam at temperatures between 100° and 300° C. were studied by determining the water absorbed and the optical properties and X-ray diffraction patterns of the products. The hydration of the probable products of decomposition under the same conditions was also studied. The main results were as follows:

Precipitated alumina, treated between 170° and 350° C. and then dried over calcium oxide or "dehydrite" at 21° C., gives a monohydrate of alumina. The product is the same whether the initial alumina contains excess combined water or has been dehydrated at any temperature below about 920° C. On similar treatment between 100° and 170° C. precipitated ferric oxide loses its water of hydration, giving a material with the crystalline structure of hematite. Tricalcium aluminate at temperatures between 150° and 300° C. forms the isometric hexahydrate.

On prolonged exposure between 100° and 300° C., dicalcium ferrite is completely decomposed to calcium hydroxide and ferric oxide (hematite). The first step appears to be a rapid direct hydration of the dicalcium ferrite to a dihydrate, followed by a rapid liberation of one mole of calcium hydroxide. Then follows a slow decomposition of the hydrated monocalcium ferrite with the formation of hematite.

Similar treatment of tetracalcium aluminoferrite at temperatures from 100° to 300° C. gives as final products the hexahydrate of tricalcium aluminate, calcium hydroxide, and ferric oxide (hematite). Here again a very rapid action appears to take place, producing the hexahydrate of tricalcium aluminate and hydrated monocalcium ferrite, the latter product then decomposing slowly to calcium hydroxide and ferric oxide as in the case of the dicalcium ferrite.

Introduction

The study of the hydration of substances present in Portland cement clinker has been mainly confined to the action of water on the silicates and the aluminates of calcium. Lately it has been shown that a compound of the composition $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ (tetracalcium aluminoferrite) is present in Portland cement (2, 3) and probably present in aluminous cements. Another compound containing iron, dicalcium ferrite, is also probably present, possibly in solid solution with tetracalcium aluminoferrite, in aluminous cements (8) and in cements of the Portland type where the alumina is to a large extent replaced by ferric oxide, as in iron ore (Erz) cement. The experiments here reported were undertaken as a part of a general study of the reactions which occur when cement mortars are cured in saturated steam at high temperatures (4, 11, 12, 13, 14), and deal with the action of steam on dicalcium ferrite, tetracalcium aluminoferrite, and on some of the possible products of hydrolysis of these.

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The available information on the hydration of dicalcium ferrite and tetracalcium aluminoferrite refers to room temperature or in some cases to a constant temperature of 30° C. Lerch and Bogue (6) found that dicalcium ferrite hydrolyzes in all solutions of calcium hydroxide that are less than saturated, and is completely hydrolyzed when exposed to water under conditions which effect the removal of the lime liberated. Kühl and Wang (5) came to the conclusion that, when finely ground cement clinker containing dicalcium ferrite is shaken with saturated limewater at room temperature, no reaction occurs, while tetracalcium aluminoferrite under the same conditions forms hydrated tricalcium aluminate and hydrated monocalcium ferrite. Since the completion of the work reported in this paper (9), Bogue and Lerch (1) report that on hydration of dicalcium ferrite in the form of a water paste, stored for long periods at room temperature, an amorphous dicalcium ferrite hydrate is probably formed and that no free lime appears. The same authors report that tetracalcium aluminoferrite under similar conditions of hydration forms the hexahydrate of tricalcium aluminate and an amorphous phase, which they conclude is probably hydrated amorphous monocalcium ferrite.

Experimental Procedure

Small samples of the materials, usually in the anhydrous form, were weighed into covered platinum crucibles. These, carefully protected from dripping water, were heated in saturated steam in autoclaves. For the higher temperatures the steel autoclave was similar to that used by Morey (7). The heating element of chromel wire was wound on the insulated autoclave, the temperature was measured by means of standardized copper-constantan thermocouples and the temperature control was effected by a choke coil. After a period of treatment the crucibles were removed to a vacuum desiccator over calcium oxide or other drying agent until constant in weight. The steam treatment and drying were then repeated until no further change in weight was noted. Very great precautions were taken against any possible contamination of the material with carbon dioxide.

Experimental Results

For the interpretation of the experimental results obtained with dicalcium ferrite and with the compound $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, it was necessary to study the behavior of the possible decomposition products in steam under corresponding conditions.

Calcium Oxide

Pure calcium oxide exposed to saturated steam at 150° C. hydrates quantitatively to the monohydrate (10). It was found that the same applies for all temperatures up to 300° C., the highest temperature used.

Alumina

Aluminum hydroxide was precipitated from a 2% solution of ammonia alum which was free from iron, the precipitate washed free from sulphate, redissolved in hydrochloric acid, and the precipitation and washing were

repeated. After this material was dried and ground to pass a 200 mesh sieve it contained 37% water (anhydrous basis). Exposure of this sample without further treatment to steam in the autoclave reduced the water held to one mole. The precipitated alumina after ignition to constant weight at temperatures up to 920° C. gave, on exposure to saturated steam in the autoclave at temperatures up to 350° C., a product of the same constant composition. For a large series of such experiments the maximum variation in the $H_2O : Al_2O_3$ ratio, after the product was dried to constant weight over calcium oxide, was from 1.01 to 1.06. This monohydrate of alumina did not lose any water when exposed for a month in vacuum over magnesium perchlorate trihydrate (aqueous tension $< 2 \times 10^{-3}$ mm.). The well defined X-ray powder pattern is identical for samples of the monohydrate produced in saturated steam at 150° C. and at 350° C. The readings of the pattern are given in Table I. This monohydrate of alumina thus appears to be a well defined compound. When the precipitated alumina was ignited to constant weight at 1100° C. it became very unreactive in steam.

TABLE I
READINGS OF X-RAY POWDER
PATTERN FOR THE MONO-
HYDRATE OF ALUMINA
(FORMED IN STEAM)

Planar spacings	Estimated intensity
6.0	SS
3.14	SS
2.81	WW
2.34	SS
1.978	W
1.850	SS
1.765	W
1.655	M
1.523	M
1.445	S
1.382	M
1.307	S
1.210	W
1.175	W
1.156	W
1.131	W
1.110	WW
1.050	WW
1.018	WW

Ferric Oxide

This was prepared by triple precipitation of the hydroxide from a solution of ferric chloride. The final precipitate, dried at 105° C., had a composition represented by $Fe_2O_3 \cdot 1.12H_2O$. On further drying over calcium oxide, the material lost about half a mole of water very quickly, but still retained somewhat more than half a mole after drying in vacuum over lime for 30 days. When the material having the composition $Fe_2O_3 \cdot 1.12H_2O$ was exposed to saturated steam at 100° to 170° C., with subsequent drying over calcium oxide, water was lost until the molar ratio of $H_2O : Fe_2O_3$ was 0.20 or less. Similar results were obtained when the material after the steam treatment was dried at 21° C. over a saturated solution of potassium chloride (aqueous tension 16.1 mm.) as when dried over calcium oxide. A good X-ray powder pattern of the steam treated material was obtained and found to be identical with the pattern given by Hansen and Brownmiller (2) for hematite. The precipitated ferric hydroxide after ignition to constant weight at 1100° C. did not take up an appreciable amount of water when exposed to steam in the autoclave.

Tricalcium Aluminate

The hydrate formed when this substance is exposed to saturated steam at 150° C. has the composition $3CaO \cdot Al_2O_3 \cdot 6H_2O$ (11). The X-ray powder pattern for this hydrate is also known (12). It was found that temperatures

of steam treatment up to 300° C. gave the same compound as shown by the amount of water absorbed, the optical properties, and by the X-ray powder pattern.

Dicalcium Ferrite

This substance was prepared by heating an intimate mixture of calcium carbonate and ferric oxide in the proper proportion well below the dissociation temperature for dicalcium ferrite, 1436° C. The material, which contained no free lime after the heat treatment, was ground to pass a 200 mesh sieve.

The platinum crucibles containing the samples of dicalcium ferrite were ignited to constant weight at 1100° C. before exposure to steam in the autoclave at temperatures between 100° and 300° C. In some cases, instead of placing the dry ignited material in the autoclave, the samples were wetted with distilled water, in other cases with a saturated solution of calcium hydroxide. The final products in every case were the same, but the reaction was more rapid when the liquid phase was present. The higher temperatures also favored the reaction.

The maximum number of moles of water held per mole of $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ after steam treatment and drying over lime at room temperature was as follows: four samples treated at 100° C. for 46 days held from 2.00 to 2.02 moles of water. Six samples treated at 170° C. for 6 to 15 days held from 2.00 to 2.03 moles of water. Three samples treated at 300° C. for 5 to 9 days held from 1.96 to 1.99 moles of water.

The absorption of two moles of water per mole of dicalcium ferrite might be due to direct hydration to a dihydrate, or complete hydrolysis to calcium hydroxide and ferric oxide, or to partial hydrolysis, possibly with hydration of the products. Three methods were used to decide this question, namely: microscopic examination, determination of free lime in the product of hydration, and comparison of the X-ray diffraction patterns of the hydration product with those of calcium hydroxide and hematite.

The hydrated material examined under the microscope showed a number of plate-like crystals which were identified as calcium hydroxide. White's test for lime was positive and the procedure of Lerch and Bogue gave two moles of free lime per mole of the original dicalcium ferrite. Further, the hydration products gave good X-ray diffraction patterns, showing only the lines found in the patterns for calcium hydroxide and steam treated precipitated ferric hydroxide.

Four samples of dicalcium ferrite after exposure to steam at 100° C. for 46 days were placed for 141 days over a saturated solution of potassium chloride at 21° C. (vapor tension 16.1 mm.). The amount of water held varied from 2.61 to 3.01 moles per mole of the original substance. It has been shown that calcium hydroxide formed by direct hydration of lime (ignited calcium carbonate) in water vapor is capable of adsorbing large amounts of water (10), and it is probable that the same applies to both the

calcium hydroxide and the hematite formed under the conditions of these experiments. Subsequent drying of the samples for four days over calcium oxide brought the water content down to 2.00 or 2.02 moles.

The experimental work therefore indicates that the final products obtained on exposing dicalcium ferrite to saturated steam at temperatures between 100° and 300°C. are calcium hydroxide and anhydrous ferric oxide (hematite).

The above gives evidence only as to the final state of the system after long periods of steam treatment. There still remains the possibility that the dicalcium ferrite is first hydrated or partly hydrolyzed and hydrated, and that the complete hydrolysis represents a slow secondary reaction. A series of experiments was made in steam at 150° C.; the time of exposure to steam was varied, and both the free lime liberated and the amount of water held after drying over lime were determined. The dicalcium ferrite was in each case ignited to constant weight at 950° C. and moistened with saturated limewater before exposure to steam in the autoclave. The results are given in Table II, each value being the average of duplicates. (Allowance was made for the free lime added as limewater.)

TABLE II
TREATMENT OF DICALCIUM FERRITE IN SATURATED STEAM AT 150° C.

Time in autoclave, hr.	Molar ratio $\text{H}_2\text{O} : 2 \text{CaO} \cdot \text{Fe}_2\text{O}_3$ after drying to constant weight over CaO	Molar ratio,
		$\frac{\text{CaO (free)}}{2 \text{CaO} \cdot \text{Fe}_2\text{O}_3 \text{ (original)}}$
4	1.73	0.97
6	1.91	1.07
12	1.94	1.29
24	1.94	1.38
62 (at 170° C.)	2.00	1.98

From Table II it is seen that nearly one mole of free lime (determined by the Lerch and Bogue procedure) is liberated on four hour treatment of the dicalcium ferrite in saturated steam at 150° C. The amount of water held by the product (after drying over calcium oxide) is much in excess of that accounted for by the free lime, so that one must assume that there was another stable hydrate present, probably $\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Microscopic examinations of the hydration products disclosed the presence of fairly large hexagonal plates of calcium hydroxide. The "four hour" sample showed a few of these present, together with dark masses which appeared to be amorphous. The X-ray diffraction pattern (23½ hr. exposure in the General Electric multiple powder apparatus) showed some *extremely* faint lines which appeared definitely to belong to the patterns for anhydrous dicalcium ferrite and calcium hydroxide. This indicated that almost all the dicalcium ferrite had been transformed at the end of the four hour treatment. The X-ray diffraction pattern for the "12 hour" sample gave a strong pattern for hematite and calcium hydroxide. The rapid liberation of the first molecule of lime and the long

time required for the liberation of the second molecule with the simultaneous formation of hematite indicates two distinct reactions. The fact that the "four hour" sample gives only a very weak X-ray diffraction pattern for hydrated lime is probably to be explained by the rapidity of the first reaction, the lime liberated not having yet formed to any great extent large enough crystals to give a pattern.

It seemed desirable to study the progress of the reaction during the first four hour period of steam treatment. A number of experiments were made with exposures in the autoclave of one, two, and four hours, the products being dried to constant weight over lime, and the water held and the free lime present being determined. The results obtained were somewhat erratic probably owing to the fact that the time required to raise the temperature of the autoclave to 150° C. and to cool it to room temperature was somewhat long and the conditions could not be controlled closely; suspended transformation also probably played a part. Thus sometimes the one hour treatment gave a greater effect than another two hour treatment. However, the results indicated rather conclusively that a large amount of hydration may take place before any lime is liberated. Thus in one case no free lime had been liberated at the end of one hour treatment at 150° C., although the material held 1.6 moles of water after drying to constant weight over calcium oxide at 21° C. In another case at the end of two hours 1.84 moles of water were held, while only 0.14 moles of free lime were present. At other times the amount of free lime was as high as 0.59 moles after a one hour treatment and as high as 0.80 after a two hour treatment, while the amount of water held varied from 1.5 to 1.85 moles per mole of original dicalcium ferrite.

It would thus appear that when dicalcium ferrite is exposed to saturated steam at 150° C. the following three reactions occur.

- (1) $2\text{CaO} \cdot \text{Fe}_2\text{O}_3 + 2\text{H}_2\text{O} \longrightarrow 2\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
- (2) $2\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O} \longrightarrow \text{Ca}(\text{OH})_2 + \text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
- (3) $\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} \longrightarrow \text{Ca}(\text{OH})_2 + \text{Fe}_2\text{O}_3 \text{ (hematite)}$

These reactions may overlap to some extent, but the third reaction is probably always slow as compared with the other two. The final products obtained are the same for all temperatures between 100° and 300° C.

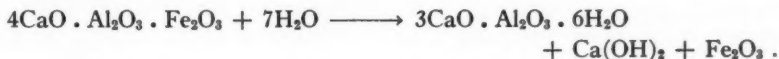
Tetracalcium Aluminoferrite

This substance was prepared by heating an intimate mixture of pure calcium carbonate, precipitated alumina, and precipitated ferric oxide in the required proportions at somewhat below 1400° C. until a uniform product, in which free lime was absent, was obtained. The refractive indices and other optical properties checked with those given by Hansen, Brownmiller, and Bogue (3). The product was ground to pass a 200 mesh sieve.

The platinum crucibles containing the samples were ignited at 1100° C. to constant weight before exposure to steam in the autoclave. Moistening the sample before steam treatment accelerated the absorption of water by the material.

Samples were exposed to saturated steam at four temperatures, namely, 100°, 150°, 170°, and 300° C. The final amount of water taken up and held after drying over quicklime was the same at all temperatures, namely, 7.04 to 7.13 moles of water per mole of original $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. Microscopic examination of the product showed the presence of two crystalline substances, hexagonal plates with a refractive index $N_0 = 1.570$ and isotropic grains with N approx. 1.61. These therefore appear to be calcium hydroxide and the hexahydrate of tricalcium aluminate. The procedure of Lerch and Bogue gave 11.5% of free lime in the steam treated material, calculated on the basis of the anhydrous sample. This represents one mole of free lime per mole of original tetracalcium aluminoferrite. White's test for free lime made on the product dried over lime was, however, always negative. After heating the product at 500° C. for one hour this test became positive. It appears that a film of some kind protected the crystals of hydrated lime from the action of White's reagent.

From the microscopic examination, combined with the determination of the water held and the free lime in the hydration product, it appears that the reaction which takes place when the compound $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ is exposed to saturated steam at temperatures between 100° and 300° C. may be represented by:



To confirm this, an intimate mixture of the substances on the right-hand side of the equation in the proportions indicated was prepared. (The Fe_2O_3 used was precipitated ferric hydroxide which had been exposed to saturated steam at 170° C. for seven days and then dried over lime.) The X-ray diffraction pattern obtained for this mixture was found to be identical with that obtained for the hydration product of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ at 170° C. An X-ray pattern of the product obtained on exposing a sample of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ to steam at 170° C. for 30 days and then drying to constant weight over a saturated solution of potassium chloride at 21° C. (aqueous tension = 16.1 mm.) was also identical. The same applied to samples hydrated at 100° C. and then dried over potassium chloride. These products held more than nine moles of water, but on drying over quicklime the amount was reduced to seven moles.

These experiments give no evidence of the formation of hydrated monocalcium ferrite as a final product, although this substance is generally assumed to be one of the products of the hydration of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ at room temperature.

The above refers only to the end products formed on treatment of tetracalcium aluminoferrite with saturated steam for long periods of time (five days or longer). A series of experiments was also made in which the sub-

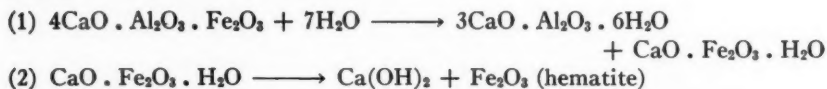
stance was exposed to the action of steam for short periods of time. Table III represents the result of one such series. The samples were moistened with saturated limewater before exposure in the autoclave.

TABLE III
TREATMENT OF TETRACALCIUM ALUMINOFERRITE IN SATURATED STEAM AT 150° C.

Time in autoclave, hr.	Molar ratio $\text{H}_2\text{O} : 4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ after drying to constant weight over CaO	Molar ratio,
		CaO (free) $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ (original)
1	7.13	0.15
2	6.74	0.23
4	7.06	0.43
6	7.01	0.41
12	—	0.62
24	7.26	0.70
411*	7.08	0.99

* This sample was exposed to steam in the autoclave without previous treatment with limewater.

The data of Table III indicate that tetracalcium aluminoferrite absorbs seven moles of water very rapidly. The liberation of lime is a much slower process and is again comparable to the liberation of the second molecule of lime in the corresponding treatment of dicalcium ferrite. The probable interpretation is that tetracalcium aluminoferrite reacts rapidly with steam at 100° to 300° C. to form the hexahydrate of tricalcium aluminate and the monohydrate of monocalcium ferrite; the latter then decomposes slowly to give calcium hydroxide and hematite.



It is also possible that first a direct hydration of the tetracalcium aluminoferrite takes place to give a hydrate with seven moles of water.

According to this interpretation the final reaction is the same for both dicalcium ferrite and tetracalcium aluminoferrite. Furthermore, the slowness of this reaction and the marked effect of temperature in increasing the rate of liberation of lime suggests that, on hydration of these substances at room temperature with a limited quantity of water, the monohydrate of monocalcium ferrite may be stable enough to represent an end product.

The deleterious effect on the strength of Portland cement mortars, produced by prolonged treatment in steam under pressure and the existence of an optimum time interval for steam curing which becomes shorter as the temperature is raised (14), is possibly at least partially explained by the slow second reaction.

Acknowledgments

The authors wish to express their appreciation to Dr. V. A. Vigfusson for help and advice in connection with the determination of optical properties and the comparison of X-ray patterns, to Mr. P. A. Puxley for making a series of experiments on the hydration of dicalcium ferrite and tetracalcium aluminoferrite, and to Dr. A. N. Winchell of the Department of Geology at the University of Wisconsin, in whose laboratory the X-ray photographs were made.

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HYSTERESIS OF WATER VAPOR ON CELLULOSE: INFLUENCE OF AIR¹

BY F. WALKER², W. BOYD CAMPBELL³ AND O. MAASS⁴

Abstract

The amount of water sorbed from vapor by cellulose which had been previously dried was compared with that retained in equilibrium with the same atmosphere by the same sample after having been saturated. The difference between the two values was constant regardless of the presence of air within the limits 10^{-2} to 10^{-4} mm. air pressure.

The Effect of Degree of Vacuum on Hysteresis in Water Sorption by Cellulose

Introduction

Hysteresis loops extending from saturation to virtually zero relative vapor pressure have invariably been found by investigators who worked with small specimens of cellulosic material under carefully controlled conditions. In all cases moisture content values are higher during the desorption process than they are during the adsorption process for the same equilibrium relative vapor pressure.

In a recent paper Hamm and Patrick (3) have claimed that the phenomenon of hysteresis can be completely eliminated by carrying out the sorption measurements in the absence of permanent gases. These results are not explainable on the basis of the most generally accepted theory of water sorption by cellulose, so the present investigation was carried out with the object of attempting to produce a change in the magnitude of the hysteresis by changing the degree of vacuum under which the measurements were made.

Previous Work

In the case of certain artificial adsorbents such as silica gel, McGavack and Patrick (4) have attributed the hysteresis to the presence of adsorbed air, but Pidgeon (5) has recently shown that the absence of a hysteresis loop in Patrick's measurements was not due to a complete removal of air as he supposed, but to changing vapor pressure during sorption.

Patrick believes that cellulose differs from inorganic gels only in that permanent gases such as oxygen are removed from it with greater difficulty. He favors Zsigmondy's (13) explanation of hysteresis on the basis of a difference under adsorption and desorption conditions in the curvatures of the menisci of the liquids filling the capillary spaces, but this explanation is hardly applicable to elastic gels such as cellulose.

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Urquhart and his co-workers (6-12) and Campbell (1) in experiments at reduced pressures (10^{-3} mm. of mercury) were unable to reduce the hysteresis effects for cellulosic materials.

Apparatus

The apparatus was designed with a view to facilitating evacuation to very low pressures, and essentially it consisted of a cell containing a helical quartz balance connected to a source of water vapor.

A diagram of the final arrangement of the apparatus is shown in Fig. 1. The cell, water bulb, and the tubing connecting them to the trap were made of Pyrex glass obtained fresh from the manufacturers, and the inside surfaces

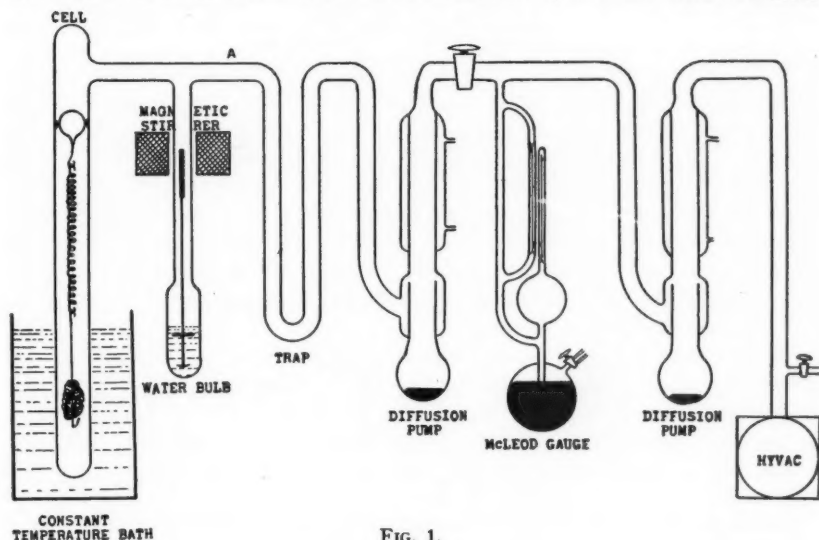


FIG. 1.

were washed once with distilled water because it was realized that glass treated with chromic acid cleaning solution presents a much larger surface for adsorption of gases.

Since speed of evacuation is limited largely by the diameter of the connecting tubing used, the cell was made of tubing of 41 mm. outside diameter and the trap and connecting parts of tubing of 22 mm. outside diameter.

A magnetic stirrer was placed in the water bulb, because continual breaking of the liquid surface hastens the attainment of vapor-pressure equilibrium. Owing to the fact that metals adsorb considerable quantities of gases, the stirrer was completely enclosed in glass.

The temperature of the cell containing the cellulose sample was thermostatically controlled at $28.00 \pm 0.05^\circ\text{C}$. The diffusion pumps used were the Cenco "Supervac" type. The McLeod gauge had a volume of 500 cc. and was calibrated to read 10^{-5} , 10^{-4} , 10^{-3} , and 10^{-2} mm. of mercury. It has been found (2) that in a system containing free mercury, small temperature

differences will cause a slow distillation of mercury, so in order to prevent condensation of mercury vapor on the sample, a trap was placed between the cell and the second diffusion pump; this trap was kept cooled by solid carbon dioxide or liquid air whenever the system was under vacuum.

The elimination of adsorbed gases from the glass tubing was an important function of the apparatus. To accomplish this, the tubing connecting the water bulb and cell to the trap was wrapped with resistance wire, as was also that section of the cell projecting above the liquid in the constant temperature bath. This enabled the apparatus to be baked out while the pumps were in operation. Only one stopcock was placed in the system, and this was done for convenience in making the low vacuum measurements.

Experimental Technique

After the apparatus had been assembled, all joints were tested for leaks with a high-frequency generator. When the apparatus was found to be free from leaks, the preliminary evacuation was carried out as follows: The water in the bulb was frozen, and the trap cooled with solid carbon dioxide; the system was evacuated until the McLeod gauge indicated 10^{-2} mm. The stopcock was closed, the ice allowed to melt and then refrozen. This procedure removed some of the dissolved air. The system was again evacuated to a pressure of 10^{-2} mm. and sealed off at *A*. The water bulb was surrounded with liquid air for 24 hr., and a reading of the extension of the balance due to the dry cellulose obtained.

Measurements of the hysteresis were carried out at this relatively high pressure. Since it was desired only to prove or disprove that the degree of vacuum has an effect on the hysteresis, it was decided to use one constant vapor pressure of water, namely that corresponding to a temperature of 0° C. This was a convenient point for two reasons. Any temperature control difficulties would be largely eliminated because the water bulb could be surrounded by a large Dewar flask containing enough chopped ice and water to last for the duration of a run. Also, the hysteresis at this relative vapor pressure amounts to a difference of about 12% in the amounts of water sorbed. This is equivalent to about 0.32% of the sample weight, and since the dry cellulose caused an extension of the balance of about 10 cm. which could be read to ± 0.001 cm., the weight of the sample was known with an accuracy of 0.01%. Under these conditions, any change in a hysteresis amounting to 0.32% of the sample weight would be readily measurable.

In order to ensure identical conditions for each run, the adsorption points were always determined with the material initially in a bone dry condition, and the desorption points with the material initially thoroughly saturated.

In making a run, the water bulb was left in solid carbon dioxide and acetone for 12 hr., and then a large Dewar flask containing ice and water was placed around the bulb. When the extension of the balance became constant within 0.01 mm. for a 10 hr. period, equilibrium was assumed to have been reached and a reading of the extension was taken. The water was removed from the bath controlling the temperature of the sample and the ice removed from

the water bulb; in this way, both sample and water were allowed to reach the same temperature. After the sample was saturated, a process that usually took about 12 hr., the temperature of the sample was again thermostatically controlled at $28.00 \pm 0.05^\circ \text{C.}$, and ice placed around the water bulb. When desorption was complete, a reading was taken as before. The difference between the two amounts of water held gave the magnitude of the hysteresis.

For the measurements under a high vacuum, the sealed-off part of the apparatus at *A* was reconnected and resistance wire wrapped around that part of the cell projecting from the constant temperature bath. The tubing of the water bulb and the tubing connecting it to the trap were similarly wrapped.

The water in the bulb was frozen and the Hyvac and one diffusion pump were started. The water was alternately frozen and melted four times under a pressure of 10^{-3} mm., so as to remove all traces of dissolved gas. Then the water bulb and trap were surrounded with liquid air, and all three pumps started. During the evacuation, current was passed through the heating coils so that the inner surfaces of the tubing were kept at about 350°C. A small section of the tubing at *A*, about 6 in. long, where the apparatus was to be sealed off, was kept at 550°C. , so that when the actual sealing off took place, adsorbed gases would not be given off to any appreciable extent. The constant temperature bath was maintained at 55°C. in order to decrease to some extent the adsorbed gases on that part of the cell under the surface of the liquid; it is generally agreed that cellulose remains unchanged at this temperature.

After 36 hr. under these conditions, the McLeod gauge indicated 1×10^{-4} mm., so it was assumed that the apparatus would be at a pressure of 1×10^{-5} at most, because of the second diffusion pump. The apparatus was sealed off at *A* and a check reading made of the extension due to the dry cellulose. Measurements of the hysteresis were made as before.

Experimental Results

TABLE I

Condition	Time allowed, hr.	Time for equilibrium, hr.	Water on sample, %	Hysteresis
<i>Air pressure, 10^{-2} mm. R.v.p., 16.15%. $T = 28.0^\circ$</i>				
Saturated	18	14	15.75	
Desorption	19	7	2.91	
Dry	32	8	0.	
Adsorption	16	4	2.59	0.32
Saturated	23	14	15.74	
Desorption	20	7	2.90	0.31
Dry	17	8	0.	
Adsorption	12	4	2.59	0.31
<i>Air pressure, 10^{-5} mm. R.v.p., 16.15%. $T = 28.0^\circ$</i>				
Saturated	26	14	15.75	
Desorption	16	7	2.66	
Dry	28	8	0.	
Adsorption	12	4	2.34	0.32
Saturated	24	14	15.75	
Desorption	13	7	2.66	0.32

Discussion

From the foregoing experimental results the conclusion may be drawn that there is no change in the hysteresis over a pressure range of 10^{-2} to 10^{-5} mm.; that is, within the experimental error, there is no effect from a thousandfold decrease in pressure.

Although Patrick (3) does not quote numerical values in his paper, he gives a graph showing the adsorption and desorption curves to be almost identical in the absence of permanent gases. However, his adsorption and desorption points at $2\frac{1}{2}\%$ moisture content differ by about 1 mm., which corresponds to 0.29% water on the scale used; this is certainly of the same order as the hysteresis in that region. Several other pairs of adsorption and desorption points at identical relative vapor pressures differ by a similar amount, and in general, Patrick's conclusion that hysteresis is eliminated seems scarcely justified by the experimental data.

In view of the present results, it seems very doubtful whether still lower pressures such as 10^{-6} or 10^{-7} mm. cause any change in the hysteresis. Any effect due to adsorbed permanent gases, at least in the amounts present in equilibrium with a pressure of 10^{-5} mm., which caused a sudden disappearance of the phenomenon of hysteresis would be difficult to explain on a theoretical basis.

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**DENSITY-PRESSURE-TEMPERATURE RELATIONS OF THE
HYDROGEN CHLORIDE-PROPYLENE SYSTEM IN THE
CRITICAL TEMPERATURE-PRESSURE REGION.
REACTION VELOCITY NEAR THE CRITICAL TEMPERATURE¹**

BY C. H. HOLDER² AND O. MAASS³

Abstract

The relation between the density, pressure, and temperature of a 2:1 and of a 1:1 mixture of hydrogen chloride and propylene has been determined over the temperature range 78° to 115° C. and up to pressures of 115 atm. These determinations are of interest in connection with the investigation of the influence of a "structure" of the liquid state on reaction velocity. Some preliminary measurements of reaction velocity in the critical temperature-pressure region have been made.

In the course of investigations (8-11) on the effect of molecular attraction on chemical reactions in the liquid state, it was observed by Maass and Sivertz (11) that a mixture of hydrogen chloride and propylene kept at room temperature and atmospheric pressure for 400 days showed no reaction. The corresponding mixture in the liquid state showed a reaction of 75% in 10 hr. at 0° C. Later, a parallel case was studied by Coffin and Maass (2, 3, 5). α - and β -Butylene reacted with hydrogen chloride in the liquid state, but in the gaseous state at 100° C. and 100 cm. pressure no reaction occurred in 40 hr.

At first sight it might be expected that the rather large difference in density between the liquid and gaseous states would be sufficient to cause or inhibit chemical reaction. With this in mind an investigation was undertaken by Sutherland and Maass (19), using the system hydrogen chloride-propylene, over a temperature range that extended well above the critical, and under pressure conditions such that the density of the gaseous mixture could be made to correspond to that prevailing in the liquid at lower temperatures. The results showed that the rate of reaction increases in a normal way in the liquid state, and that above the critical temperature the velocity of the reaction diminishes to such an extent as to introduce a discontinuity.

Largely as a result of these observations a study of the properties of substances in the critical pressure-critical temperature region was undertaken in this laboratory (6, 13, 14, 20, 22, 23). The observations made supported the hypothesis that the change from the liquid to the gaseous state involves something more than a mere change in concentration, and that in the liquid state of aggregation there exists a regularity in molecular distribution that gives to it what might be termed a "dynamic structure". Without specifying whether this "structure" takes the form of regional orientation (4, 10, 18), it is

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true nevertheless that the results of Sutherland and Maass can be explained on the basis of such a hypothesis. If the existence of a "structure" promotes the velocity of a chemical reaction, its disappearance above the critical temperature will bring about a decrease in the rate of reaction, if this means that the change to a perfectly chaotic distribution of molecules has taken place. Some recent work by A. L. Geddes (7) and the investigations of Stewart and his co-workers on X-ray diffraction (1, 15, 16, 17, 18) indicate that, while this is probably the case when the two-phase system liquid-vapor is heated to the critical temperature, under pressures greater than the critical pressure the "dynamic structure" persists above the critical temperature.

It was therefore considered advisable to reinvestigate the reaction between propylene and hydrogen chloride, and as a preliminary to determine the pressure-volume-temperature relation of this two component system both above and below the critical pressure, in the temperature region where rate measurements were planned.

Experimental

The Apparatus

The apparatus is essentially the same as that used and described by Sutherland and Maass (19) and later by Winkler and Maass (21), and for this reason will not be described in detail here. The apparatus is depicted diagrammatically in Fig. 1 (reproduced from Winkler and Maass's paper (21)). Definite amounts of the reactants, kept in storage flasks (not shown), were measured in calibrated volumes V_1 and V_2 and then transferred to P . The pressure of the mixture at a certain volume and temperature was recorded. By proper

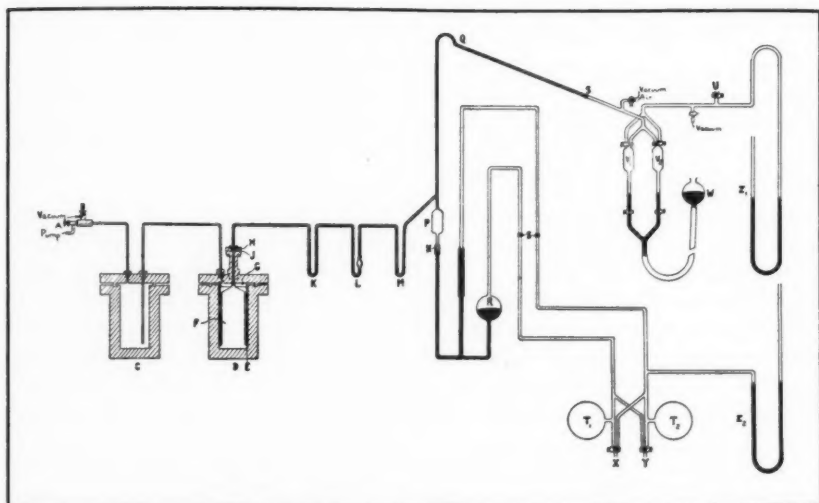


FIG. 1.

manipulation of the mercury supplies the gases were compressed into the small upper bulb of the reaction cell *L*. The gas could be kept there for any length of time by freezing the mercury in *K* and *M*. To stop the reaction the mercury seals were melted and the gases were returned to *P*, and from the pressure change observed the percentage reaction could be readily calculated.

Materials

Propylene was prepared as described by Maass and co-workers (3, 12) by the dehydration of isopropyl alcohol over alumina at 350° C. Purification was carried out by fractionating the liquid five to eight times by means of a carbon dioxide-acetone bath.

Hydrogen chloride was prepared by the action of c.p. sulphuric acid on recrystallized c.p. sodium chloride covered with c.p. hydrochloric acid. The gas was passed through four sulphuric acid scrubbers and condensed by means of liquid air. It was then fractionated, by the use of liquid air, four or five times.

Results

Densities were determined for both 2:1 and 1:1 mixtures of hydrogen chloride and propylene over a temperature range from 78° to 115° C. This was done by compressing a known weight of the reactants, measured out in the calibrated volumes V_1 and V_2 , into the small reaction bulb whose volume was found to be 0.26 cc. by calibration with mercury. The Bourdon gauge was calibrated against the vapor pressure of hydrogen chloride at pressures of 950 and 1200 lb. per sq. in. A correction of 1% subtracted from the observed reading was found necessary. For a given mixture, whose density could be calculated from the following equation, the pressure required for a number of different temperatures was determined. This was then repeated for a mixture of different density.

$$\text{Density} = \frac{p_1 M_1 + p_2 M_2}{1000 RT} \times \frac{V}{v}$$

where p_1 and p_2 are pressures of propylene and hydrogen chloride respectively in V_1 and V_2 ,

M_1 and M_2 are molecular weights of propylene and hydrogen chloride respectively,

V is the volume of V_1 and $V_2 = 93.3$ cc.,

v is the volume of the reaction bulb = 0.26 cc.,

R is the gas constant,

T is the temperature of gas in V_1 and V_2 in degrees absolute.

The results obtained are presented in Table I. Figs. 2 and 3 show pressure plotted against density for a given temperature. From these curves the density of a mixture can be determined from its temperature and pressure, even though it may not exactly fill the reaction cell. In this way the curves are of use experimentally.

TABLE I

Density	Temperature, °C.				
	78	85	95	105	115
	Pressure, atm.				
2 HCl : 1 C ₃ H ₆					
0.34	84.2	92.0	105.2	118.4	—
0.28	78.5	85.4	95.7	104.3	113.5
0.22	72.4	77.8	84.2	89.9	96.4
0.14	60.2	62.9	67.6	72.4	76.8
0.094	44.7	47.3	49.7	52.5	54.8
0.048	27.0	27.9	29.0	30.1	31.3
1 HCl : 1 C ₃ H ₆					
0.29	67.0	74.4	84.6	94.7	105.5
0.23	63.9	69.7	77.5	84.9	92.0
0.15	56.5	60.2	65.0	69.3	74.4
0.069	34.5	35.5	37.2	39.3	41.0

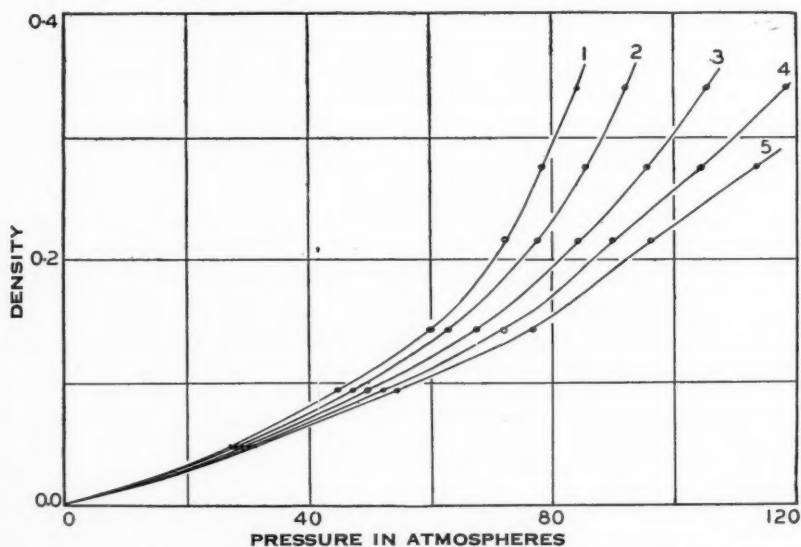


FIG. 2. Isotherms for 2 HCl : 1 C₃H₆ mixtures. 1. -78°. 2. -85°. 3. -95°. 4. -105°. 5. -115° C.

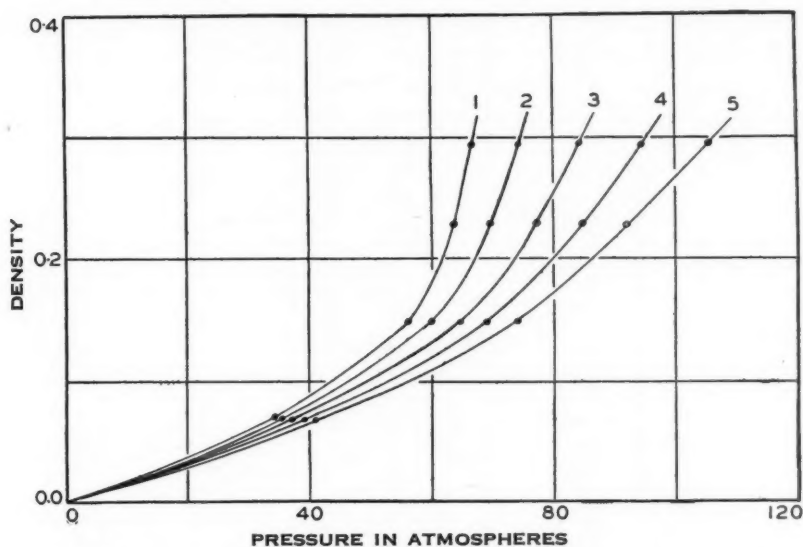


FIG. 3. Isotherms for 1 HCl : 1 C_3H_6 mixtures. 1. -78° . 2. -85° . 3. -95° . 4. -105° . 5. -115° C.

Pressure readings could be made to within 1% of the pressure and 0.1° C. of the temperature. The greatest error involved is due to the position of the mercury at the ends of the reaction cell in the constricted parts of the tubing. Duplicate measurements could be made to within 0.01 of the absolute value of a density at the highest density and 0.002 at the lowest.

A test of the accuracy of the measurements is given by plotting the relation between pressure and temperature for isosteres, which should give a constant value for $\frac{dp}{dT}$. In

Figs. 4 and 5 the straight line relation between pressure and temperature is made evident.

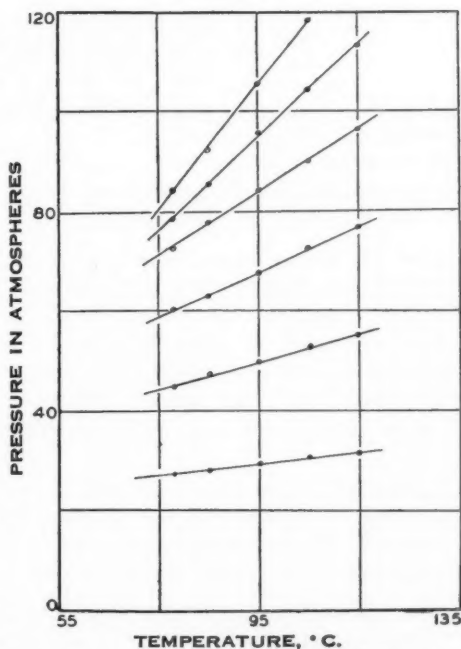
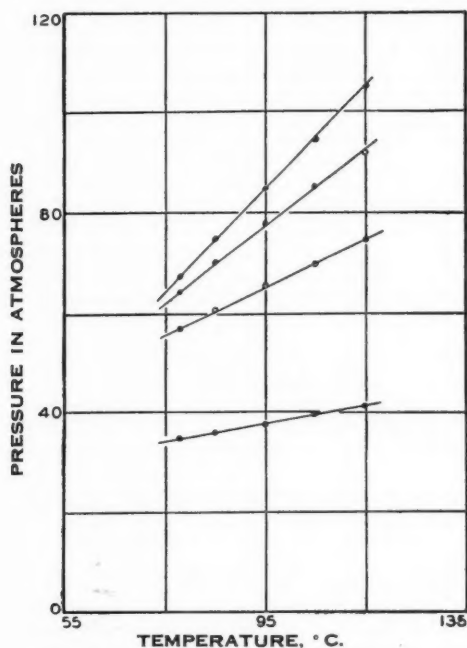


FIG. 4. Isosteres for 2 HCl : 1 C_3H_6 mixture.

FIG. 5. Isotherms for 1 HCl : 1 C₃H₆ mixture.

Discussion

Reaction Velocity Measurements

In the density measurements described, the absence of any reaction during the time that the measurements were made was confirmed by examining the pressure of the gas mixture at a constant volume before and after.

Some preliminary rate measurements have been made over a five hour period instead of the two hour period used by Sutherland and Maass. Essentially, their results have been confirmed. For instance, a 2 : 1 mixture at 105° C. and a pressure of 100 atm. in five hours showed only 2.5% reaction; when this mixture, after having been sealed in the reaction vessel at the same density was then cooled down to 50° C., a reaction of 3% in half an hour occurred. This is nine times as fast as the reaction above the critical temperature.

Sutherland and Maass found that the reaction above the critical temperature could be readily catalyzed by the presence of impurities such as traces of mercury chloride. This impurity had not been completely eliminated, and the apparatus is being renovated with this in view.

It is planned to make long time rate measurements over an extensive temperature-density range. For that purpose the data given in the first part of the paper are essential. Apart from this they are of interest

since so few accurate data are available for two component systems at high pressures, and this may be looked upon as the first of a number of two component systems to be studied in this laboratory.

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